

CHEMISTRY

for Secondary Schools

(ADVANCED EDITION)



CROAL COULKE LOUDEN
PICKARD MORRISON

CURRICULUM

Period	Group				MODERN CLASSIFICATION OF THE											
	I A		II A													
1																
2	2 1	3 Li 6.940	2 2	4 Be 9.013	TRANSITION											
3	2 8 1	11 Na 22.991	2 8 2	12 Mg 24.32												
4	2 8 8 1	19 K 39.100	2 8 8 2	20 Ca 40.08	III B	IV B	V B	VI B	VII B							
5	2 8 18 8 1	37 Rb 85.48	2 8 18 8 2	38 Sr 87.63	2 8 9 2	21 Sc 44.96	2 8 10 2	22 Ti 47.90	2 8 11 2	23 V 50.95	2 8 13 1	24 Cr 52.01	2 8 13 2	25 Mn 54.94	2 8 14 2	26 Fe 55.85
6	2 8 18 18 8 1	55 Cs 132.91	2 8 18 18 8 2	56 Ba 137.36	2 8 18 32 10 2	57-71 See Lanthanide Series	2 8 18 32 11 2	72 Hf 178.58	2 8 18 32 12 2	73 Ta 180.95	2 8 18 32 12 2	74 W 183.86	2 8 18 32 13 2	75 Re 186.22	2 8 18 32 14 2	76 Os 190.2
7	2 8 18 32 18 8 1	87 Fr (223)	2 8 18 32 18 8 2	88 Ra 226.05	89-100 See Actinide Series	NOTE "A" groups consist of elements where the outside ring carries the valence electrons. "B" groups are the transition groups where a shell other than the outermost is being filled. Vertical column to the left of the element shows ring structure. The heavy step line represents the division between metals and non-metals. The heavy vertical line separates the inert elements.										

Lanthanide Series	2 8 18 18 9 2	57 La 138.92	2 8 18 19 9 2	58 Ce 140.13	2 8 18 20 9 2	59 Pr 140.92	2 8 18 22 8 2	60 Nd 144.27	2 8 18 23 8 2	61 Pm (145)	2 8 18 24 8 2	62 Sm 150.35
Actinide Series	2 8 18 32 18 9 2	89 Ac 227	2 8 18 32 19 9 2	90 Th 232.05	2 8 18 32 20 9 2	91 Pa 231	2 8 18 32 21 9 2	92 U 238.07	2 8 18 32 22 9 2	93 Np (237)	2 8 18 32 23 9 2	94 Pu (242)

ELEMENTS SHOWING ELECTRON STRUCTURES

1

1

H

1.008

2

2

He

4.003

III A

IV A

V A

VI A

VII A

ELEMENTS						2 3	5 B	2 4	6 C	2 5	7 N	2 6	8 O	2 7	9 F	2 8	10 Ne		
							10.82		12.011		14.008		16.000		19.00		20.183		
VIII B						2 8 3	13 Al	2 8 4	14 Si	2 8 5	15 P	2 8 6	16 S	2 8 7	17 Cl	2 8 8	18 A		
							26.98		28.09		30.975		32.066		35.457		39.944		
2 8 15 2	27 Co	2 8 16 2	28 Ni	2 8 18 1	29 Cu	2 8 18 2	30 Zn	2 8 18 3	31 Ga	2 8 18 4	32 Ge	2 8 18 5	33 As	2 8 18 6	34 Se	2 8 18 7	35 Br	2 8 18 8	36 Kr
	58.94		58.71		63.54		65.38		69.72		72.60		74.91		78.96		79.916		83.8
2 8 18 16 1	45 Rh	2 8 18 18	46 Pd	2 8 18 18 1	47 Ag	2 8 18 18 2	48 Cd	2 8 18 18 3	49 In	2 8 18 18 4	50 Sn	2 8 18 18 5	51 Sb	2 8 18 18 6	52 Te	2 8 18 18 7	53 I	2 8 18 18 8	54 Xe
	102.91		106.7		107.880		112.41		114.82		118.70		121.76		127.61		126.91		131.30
2 8 18 32 17	77 Ir	2 8 18 32 17 1	78 Pt	2 8 18 32 18 1	79 Au	2 8 18 32 18 2	80 Hg	2 8 18 32 18 3	81 Tl	2 8 18 32 18 4	82 Pb	2 8 18 32 18 5	83 Bi	2 8 18 32 18 6	84 Po	2 8 18 32 18 7	85 At	2 8 18 32 18 8	86 Rn
	192.2		195.09		197.0		200.61		204.39		207.21		209.00		210		(211)		222

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Chemistry for Secondary Schools



Herb Nott

Preparing and collecting oxygen

[1162]

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Preface

"In order to lead my students to the conviction which I have reached myself, I wish to place them on the same path as that by which I arrived at it—the path that is of the historical examination of chemical theories."

S. CANNIZZARO

Chemistry for Secondary Schools is an attempt to present chemistry in an attractive and interesting manner not only to students who wish to become professional chemists, but also to the majority of high school students who will not have further formal instruction but will require some knowledge of the subject in order to have a better understanding of the modern world in which they live.

The historical approach followed in the text endeavours to show the manner in which the science has developed, in the hope that the student will be guided to reason along the same lines as the great men of chemistry have reasoned. The universality of the science of chemistry is accentuated by the study of the contributions made by men of every country. The manner in which these ideas have been accepted and interchanged should demonstrate tolerance and teach an appreciation of international good will and co-operation.

Basic principles of atomic and molecular structures are given to enable a student to retain facts without leaving himself entirely at the mercy of his memory. In every instance a clear-cut distinction is drawn between theory and fact. Many theories are discussed and reasons are given for accepting some, modifying others, and discarding those obviously outmoded by new discoveries and increased knowledge. Consistent with the aims of general education, laws are not stated and then verified; rather, evidence is collected by the pupil from his own investigations and from the records of others, and generalizations are made after the facts have been accumulated. Such treatment encourages the spirit of inquiry and develops reasoning power.

Each chapter is provided with an adequate number of questions so that the teacher can cover the work by making all assignments from them. This enables the teacher to save valuable class-room time. Model solutions are given for difficult problems.

Word equations form an integral part of the experimental work in the early chapters of the text. These are replaced by chemical equations only when sufficient understanding has been developed and the student is in a position to substitute formulae for words.

The text includes elementary ideas of the periodic classification of the elements, of atomic structure, and the electron concept of valence. Although not usually included in an elementary treatment, this material has been added for the benefit of those of more than average ability in the hope that they will be encouraged to continue the study of chemistry.

The authors gratefully acknowledge the contribution made by Mr. K. L. Wismer, M.A., head of the chemistry department at Humberside Collegiate, Toronto, for the many excellent diagrams drawn by him under their direction and supervision. They also acknowledge with thanks the many contributions so willingly made by chemical industry. Throughout the text each contribution is acknowledged with a credit line. To Canadian Industries Limited special thanks is given for permission to make full use of the wealth of material found in their literature. Thanks are also due to Mrs. A. G. Croal for typing the manuscript, and to Miss Beatrice Logan and Mr. Marsh Jeanneret for their wise counsel and constructive criticism.

A. G. C.

J. H. C.

A. H. L.

The advanced edition of Chemistry for Secondary Schools includes the complete text of the original edition by A. G. Croal, J. H. Couke and A. H. Loudon. To bring the text-book to the matriculation requirements for Alberta, additional chapters 27 to 32 inclusive were written by N. J. Pickard and J. L. Morrison.

The new chapters deal with the chemistry and metallurgy of aluminum, iron and copper and offer a brief survey of the chemistry of carbon compounds and foods. These topics are considered essential in a chemistry course which serves both as a terminal and a matriculation course.

The authors of the additional chapters wish to thank Dr. G. L. Mowat, Dr. W. E. Harris, and Mr. M. Fowler for critically reviewing the material and making many constructive suggestions. They acknowledge with gratitude the photographs and charts supplied by the Government of Alberta and the various industries indicated in the credit lines.

N. J. P.

J. L. M.

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Chemistry for Secondary Schools

CHAPTER 1

Chemistry: A Science

Surely to alchemy this right is due, that it may be compared to the husbandman whereof Aesop makes the fable; that, when he died, told his sons that he had left unto them gold buried in his vineyard; and they digged all over the ground, and gold they found none; but by reason of their stirring and digging the mould about the roots of their vines, they had a great vintage the year following: so assuredly the search and stir to make gold hath brought to light a great number of good and fruitful inventions and experiments.

FRANCIS BACON

The age of alchemy. As the Arabs spread their control over the Mediterranean world, they carried with them much of the knowledge they had acquired from the Egyptians and Greeks. To the magical secret practices of the Egyptians they applied the word **alchemy** (EGYPT. *khemet*, dark, black), from which the word **chemistry** was derived later.

Among other things, these early alchemists knew how to prepare drugs, to dye cloth, to make soap and glass, and to extract metals from their ores. The European alchemists, however, soon turned their attention to a problem that was to concern them for fifteen centuries. It was thought that metals grew like plants and, like living things, could become ill. Gold was considered to be the only "well" metal, and baser metals were believed to be gold in various stages of "sickness". Therefore, the alchemists reasoned that, if the growing methods of metals could be discovered and the "sick" metals made well, gold could be made from any of the baser metals. This **transmutation** was to be brought about by the discovery of a substance, commonly referred to as the "philosopher's stone", which when added to a baser metal would change it into gold. As one generation succeeded another, new properties were assigned to this mythical substance by means of which alchemists hoped to be able to prolong life,

to change cowards into heroes, to make the old young, and even to revive the dead. In attempts to reach this unattainable goal, alchemists

worked long hours in small dingy rooms heating, mixing, dissolving, distilling and treating materials by every known method including the sing-song chant of incantations.

Many alchemists were sponsored by kings and nobles who longed for the power gold would bring. These alchemists were both feared and respected by their superstitious patrons who lacked knowledge of what concoctions might be brewing in those steaming caldrons.

The alchemists also sought to discover a "universal solvent" (the alkahest), but gave little thought to the question of a container for such a unique liquid.

In the latter part of the sixteenth century, alchemy became allied with medicine when the alchemists came under the influence of the Swiss physician Paracelsus who declared alchemy's true purpose was the preparation of medicines rather than the making of gold. Giving up their search for the philosopher's stone, the alchemists directed their efforts to control of the terrible plagues exacting a heavy death toll and sought an *elixir vitae* (elixir of life) which would cure all diseases. Paracelsus studied the properties of substances and began a scientific investigation that laid the foundation for the work of the great chemists of the seventeenth and eighteenth centuries.

Obviously, during a period of fifteen hundred years, the alchemists



Fig. 1.1. Robert Boyle (1627-1691) began the scientific method.



Fig. 1.2. Paracelsus (1493-1541), a Swiss physician and alchemist.

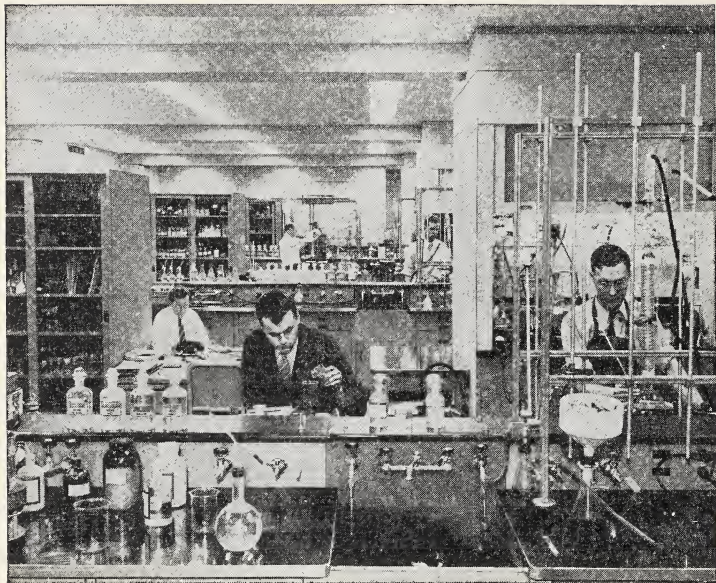
*Fisher Collection*

Fig. 1.3. The Alchemist, by David Teniers.

used nearly every known ingredient in their preparations, but they were unable to classify this knowledge accurately or to use it extensively in their search for new facts.

The great names of early chemistry. Modern chemistry may be said to have begun about the middle of the seventeenth century when the search for mythical substances came to a close, but many years passed before the "new" science was put on a sound footing. Near the end of the century, Robert Boyle introduced a method of study that has been closely followed ever since. His was the method of experiment whereby experimental facts, established by careful observations, became the bases for conclusions. Using Boyle's inductive method, such men as Priestley, Cavendish, Scheele, Lavoisier, and Dalton classified the knowledge of the alchemists and laid the foundations for chemistry as a true science.

Although hampered by antiquated laws, hindered by public reverence for ancient traditions, and obstructed by popular superstition and fear, these men and others like them refused to be discouraged. They made possible the scientific development of a new age and to them we owe many of the amenities of modern living.



B. F. Goodrich

F'g. 1.4. A modern research laboratory.

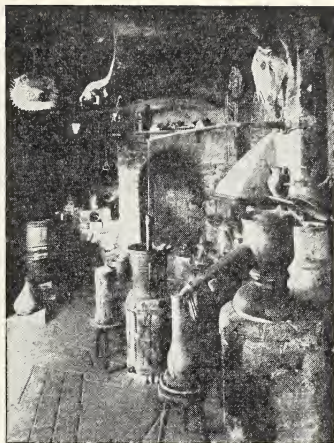
Chemistry today. The science of chemistry contributes to the security and pleasantness of practically every phase of modern life. Chemistry helps to make possible for us the homes we live in, the motor cars we drive, the pure water we drink, and the clothes we wear. Through chemical processes, pulpwood is converted to "cellophane" or rayon or newsprint; textiles are bleached or coloured; paints are compounded; and explosives manufactured to make possible highway and railway construction. Through chemistry, rubber is adapted to many uses and "neoprene", a man-made rubber to serve particular purposes, is manufactured. Chemistry is responsible for plastics, those colorful, light-weight materials of many uses. Because of chemistry, our clothing can be water-proofed and leather transformed into soft, comfortable shoes. We enjoy these and other advantages largely because a few men through the ages have struggled and suffered in order that science may serve the whole of mankind.

What is chemistry? Every high school pupil possesses some scientific knowledge. He knows something about physics, chemistry, biology, geology and other branches of science, but his ideas of the meanings

of these terms may be vague because of unorganized knowledge. The few books in a home library may be arranged in any order, but definite organization is necessary in a library of one hundred thousand volumes. Arrangement or organization is unessential in infancy when ideas are few. However, as "knowledge grows from more to more", learning demands arrangement, organization, and classification if it is to have the highest value. In the past, many schemes of organization have been tried and abandoned. Today, the simplest and most satisfactory scheme is to group all knowledge under the broad general term *science*.

Because of the vastness of this subject, science is subdivided into many sections, each of which in turn deals with a distinct part of human knowledge. Thus, mathematics is the science of numbers and quantities; biology is the science of living things; physiology is the study of how the body functions; and psychology is the study of the mind.

Chemistry is the science that deals with matter and those changes in which matter is converted from one substance to another.



Fisher Scientific Company

Fig. 1.5. Tools of the alchemist were a far cry from modern scientific apparatus. His crude implements invoke a respect for his patience and perseverance.

EXERCISE

1. Explain why the reference made to alchemy by Bacon is particularly applicable.
2. What did the alchemists hope to accomplish with (a) the philosopher's stone, (b) the universal solvent, (c) the elixir vitae?
3. Did the alchemists achieve anything of value? Discuss.
4. Although it made many contributions, alchemy is not regarded as a science. Why?
5. What is meant by the transmutation of an element? What has been accomplished by modern chemists in the field of transmutation?
6. What effect did the influence of Paracelsus have on the activities of the alchemists?

7. What important contribution by Robert Boyle helped to lay the foundations for chemistry as a true science?

8. Give the derivation and the meaning of the word *chemistry*.

9. Name five outstanding men (other than Paracelsus and Boyle) who contributed to the establishment of chemistry as a science. By further reading, discover what these contributions were.

10. List twelve ways in which chemistry has contributed to your pleasure and security.

CHAPTER 2

Physical and Chemical Changes

Most of the substances belonging to our globe are constantly undergoing alterations in sensible qualities, and one variety becomes, as it were, transformed into another. Such changes, whether natural or artificial, slowly or rapidly performed, are called chemical.

SIR HUMPHRY DAVY

Matter and its states. Anything that occupies space or has weight is matter. This includes not only solid and liquid substances such as wood and water, which can be seen and touched, but also various invisible gases such as air and carbon dioxide. To name all the substances in the world would be impossible but a simple classification can be attempted. Matter exists in one of three physical states: solid, liquid, or gas. A solid is rigid and has definite volume and shape. A liquid flows, has definite volume but no definite shape, and assumes the shape of the containing vessel in which it rests in as far as it fills it. A gas has neither definite volume nor definite shape. A gas always tends to expand so as to fill entirely any vessel in which it is placed.

Changes in state. It is possible to change a substance from one state to another by changing the conditions under which it is maintained. These transformations are often brought about by changes in temperature and pressure. Many substances occur in any or all of the three states mentioned, the particular state being dependent on the temperature and pressure conditions. Water at its freezing point changes to ice on a further removal of heat. Water at the boiling point changes to steam on the application of more heat. Conversely, solid ice, when subjected to heat, becomes a liquid and is said to **melt**. If heat be removed from steam that is at the boiling point, the steam condenses into water. Most substances can exist in all three states if either temperature or pressure, or both, are appropriately altered. Under ordinary conditions, air is a gas, but if adequately cooled and subjected to sufficient pressure it becomes a liquid or even a solid. When a solid is transformed to a liquid, the change is called melting, or **fusion**. When a liquid is transformed to a solid, the change is called **freezing**, or **solidification**. Liquids may vaporize to gases in two ways,

evaporation and boiling, either process being referred to as **vaporization**. The term **vapour** is used to refer to the gaseous state of any substance which normally exists as a liquid. Water, exposed to air at any temperature, evaporates at its surface and so dissolves in the air. The action whereby steam is formed throughout an entire mass of water is **boiling** and the temperature at which this change occurs is

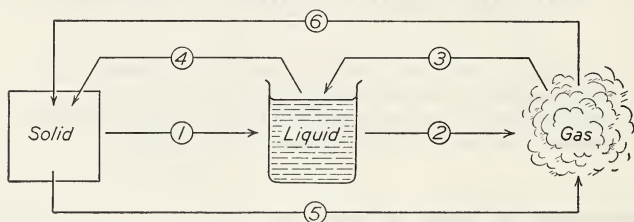


Fig. 2.1. Diagram to illustrate changes in state. 1, melting. 2, vaporization. 3, condensation. 4, freezing (solidification). 5 and 6, sublimation.

called the **boiling point**. When a gaseous substance, through loss of heat, changes to a liquid, the process is called **condensation**. At below freezing temperatures, snow may sublime directly into the air without experiencing any intervening state. Conversely, water vapour in the air may sublime or solidify directly to frost or snow. Such a direct change from solid to gas, or from gas to solid, or both, is called **sublimation**.

The accompanying diagram shows the relationship of these changes in the states of matter. It should be noted that the only changes shown have been changes of state. None of these transformations have produced any new substances.

Properties of matter. Because no two fingerprints are identical, the expert, through study and a system of classification, can identify any single print. Since the chemist deals with many kinds of matter, he must have some method of identifying and classifying each. Chemists use the word **properties** to indicate the characteristics or qualities of a material whereby they can identify it and determine its uses. As with people and fingerprints, no two chemical substances have identical properties.

Physical properties. In dealing with the subject of chemistry, expressions such as **physical properties** and **physical change** will frequently occur. A geologist, studying the remains of bygone eras, finds the remains of animals and plants in rocks and is compelled to bring to his study of geology some knowledge of zoology and botany.

Similarly, many facts belonging to the realm of physics, are essential to the study of chemistry. Such characteristics as state, odour, taste, lustre, solubility in water or other solvents, density, hardness, malleability, ductility, melting point, boiling point, and any other characteristics used in the identification of a substance are known as physical properties.

A chemist, examining any specimen of pure iron under ordinary conditions, finds that it is always a grey solid with a bright lustre, that its specific gravity is 7.85, that it melts at $1530^{\circ}\text{C}.$, that it has toughness, malleability, ductility, can be magnetized, etc. These are some of the physical properties of iron that collectively help to distinguish it from any other substance.

Physical change. If an iron ball is converted into a pile of filings, the resultant change is one of form only. If the iron ball is melted, the change is still one of state only. In each instance, the change of form in no way affects the original properties of the substance, which remains iron.

Similarly, the sawing of wood, the breaking or bending of glass, the crushing of rocks, the magnetization of iron, the formation of dew, and the heating of platinum wire, are examples of alterations whereby the materials concerned lose none of the characteristics by which they are identified. They remain substantially the same throughout although their physical properties may be temporarily altered.

Any change in the original substance that does not result in the production of a new substance is called a physical change.

Chemical properties. The chemical properties of a substance can be determined by observing its action, or lack of action, when it is placed in contact with other substances. Chemical properties also include the behaviour of a substance when it is heated, or exposed to light, or decomposed by the passage of an electric current. Thus, when we state that hydrogen burns, or that oxygen supports combustion, we are referring to chemical properties of these two gases.

Chemical change. When a chemical change occurs in a substance, the substance loses its identity. The new substance or substances resulting from the change have different physical and chemical properties, as well as a different energy content, from the original material. A chemical change is usually accompanied by a change in temperature.

The rusting of iron, the burning of coal, the creation of starch and sugar by green plants, the digestion of food, and the decomposition of water into oxygen and hydrogen by means of the passage of an electric current, are examples of familiar changes. It is quite evident that the

products of these processes possess properties totally different from those of the original materials. Thus, when a piece of coal burns, the resulting ash and gases have different properties from the original coal, and lack the energy content of the coal in that neither of the newly formed products can be burned to give heat.

Any change in the original substance that results in the production of a new substance or substances with properties totally different from the original is called a chemical change.

In the following chapters, scores of additional examples of chemical changes will be encountered.

EXERCISE

1. (a) What is matter? (b) Name the three states of matter. (c) What factors regulate these three states?
2. Give the distinguishing characteristics of each state of matter.
3. What change of state takes place when (a) a dense fog appears, (b) moth balls in stored clothing disappear, (c) a large volume of air is changed to liquid air, (d) melted fat is stored in a refrigerator?
4. Define each of the following terms and give an example of each: vaporization, condensation, liquefaction, solidification, sublimation.
5. Distinguish between evaporation and boiling.
6. (a) Why is a knowledge of the properties of matter important? (b) List ten physical properties and five chemical properties often used in identifying various substances.
7. (a) How does a physical change differ from a chemical change? (b) Are chemical changes always accompanied by physical changes? Discuss.
8. Which of the following changes are physical and which are chemical? Give convincing reasons in each case: magnetizing a nail; the fermentation of cider; the glowing of a neon sign; toasting a piece of bread; the disappearance of fog; melting iron in contact with air; dissolving sugar in coffee; the drying of damp clothes; the drying of house paint; fallen leaves decay; the tarnishing of silver; lighting a match.
9. Give five examples of physical changes and five examples of chemical changes other than those mentioned in this chapter.

CHAPTER 3

The Scientific Method

Phlogiston died as an old king—once infinitely dominant, somewhat tyrannical, not always just; now deposed, decrepit, utterly senile, forsaken by all.

W. ODLING

The phlogiston theory. Man has always been curious about fire, and it is not surprising that the early chemists attempted to explain the nature of burning or combustion. In 1669, Johann Becher wrote a book in which he tried to answer the question, "What really happens when a substance burns?" Becher put forward a theory that all combustible materials contained a "fatty earth" he called *terra pinguis* and that, when burning took place, the *terra pinguis* escaped with the flame.

George Ernst Stahl (1660-1734), a pupil of Becher, developed his teacher's views and advanced a theory that lasted for more than a century. Stahl dropped the name *terra pinguis* and propounded the theory that a substance **phlogiston** (from a Greek word meaning *fire-stuff*) was present in all combustible substances, and that phlogiston escaped when a substance burned. Exceedingly combustible substances were believed to contain much phlogiston, but the ash remaining after combustion contained no phlogiston and hence would not burn.

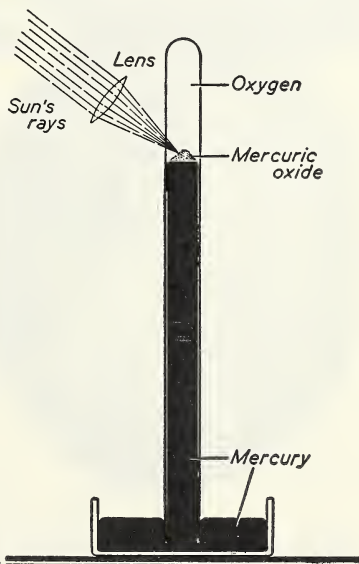


Fig. 3.1. With a similar apparatus Priestley discovered oxygen.

Incombustible substances contained no phlogiston. The phlogiston theory was so strongly advocated by such eighteenth century chemists as Cavendish, Priestley, and Scheele that it became thoroughly established.

Stahl, however, had advanced a theory without paying due regard to all the facts, and without having made actual measurements. His theory had two faults: first, no one had ever seen, caught, or weighed phlogiston free from the substances supposed to contain it; second, no one had ever examined the air to discover what changes had occurred in it during the burning process. In other words, Stahl brought forward no experimental proof of his theory. Later it was discovered that the weight of the residue left after a metal burned was greater than the weight of the metal before burning. This discovery could not be explained on the basis of the phlogiston theory because the loss of phlogiston should have resulted in a decrease in weight. Stahl's followers attempted to explain this discrepancy by saying that phlogiston possessed a so-called "negative weight" that decreased the weight of any substance containing it.

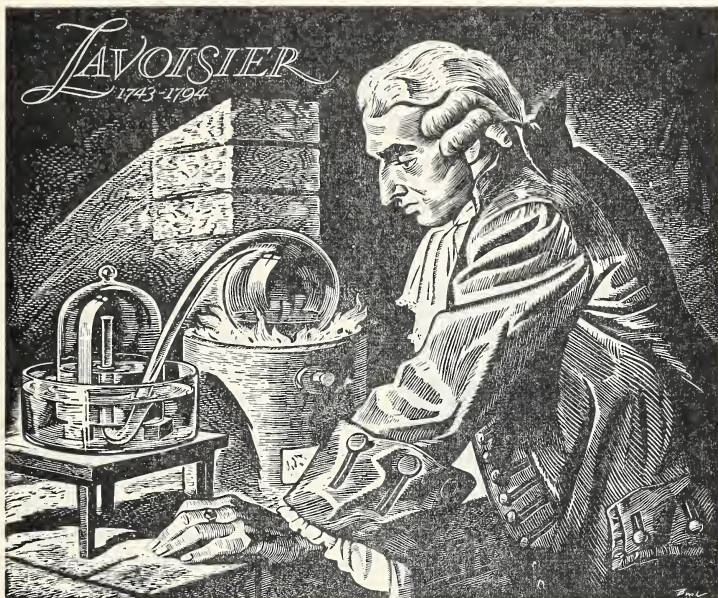
The phlogiston theory of combustion was only rejected when scientists learned to study facts first and formulate their theories afterwards.

The modern theory of combustion. One of the greatest of the phlogistonists was Joseph Priestley, an English preacher, who studied chemistry as a hobby. He was a great experimenter and was constantly heating substances in attempts to produce new gases which he called "airs". As a source of heat, Priestley frequently used a lens to concentrate the rays of the sun on the materials being heated. The gases produced were collected in bottles in a pneumatic trough, one of Priestley's inventions. Con-



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Fig. 3.2. Karl Wilhelm Scheele (1742-1786), a Swedish chemist, was probably the first chemist to prepare pure oxygen. He discovered a great number of new substances including chlorine.



International Nickel

Fig. 3.3. Antoine Laurent Lavoisier (1743-1794) the, "father of modern chemistry".

cerning one of his experiments he wrote: "I proceeded with great alacrity to examine by the help of it (a lens) what kind of 'air' a great variety of substances, natural and fictitious, would yield, putting them into vessels filled with quicksilver (mercury) kept inverted in a basin of the same" (Fig. 3.1).

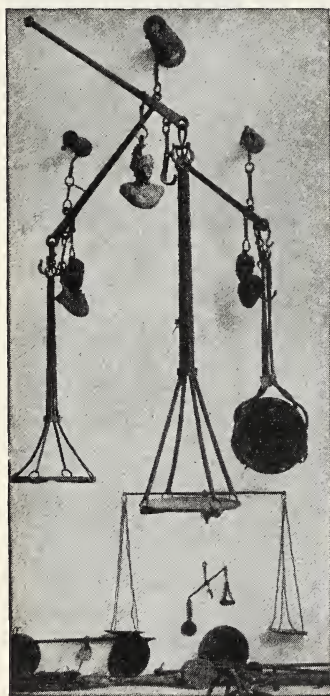
In 1774, while heating one of these substances, red calx, or "mercurius calcinatus per se" (mercuric oxide), Priestley discovered a gas we now know as oxygen. He erroneously believed that this new gas was the one in the atmosphere with which phlogiston combined when it escaped from a burning substance. He therefore called it "dephlogisticated air", meaning a gas devoid of phlogiston. Because Priestley was so sure that something was given off during the burning process, he missed the real significance of this discovery due to inadequate investigation of his findings.

It remained for a famous Frenchman, Antoine Laurent Lavoisier (1743-1794), to advance a new theory of combustion. He was the first chemist to recognize the fact that the chemical balance should be the

first resort in all chemical investigations. A hundred years earlier John Mayow, an English physician, had discovered that there was a diminution in volume of the air resulting from breathing and burning. About 1770, Karl Scheele had shown that the active part of the air could be removed by the rusting of iron, the smouldering of phosphorus, and other methods.

In 1774, Lavoisier weighed a sealed glass flask containing tin and air. He heated this for several days and found that a white powder had formed on the tin but that the flask and its contents had not changed in weight. He then made a hole in the flask and on re-weighing the flask and its contents he found that the weight had increased. Further investigation showed that this increase in weight was the same as the increase in weight the tin had undergone when it was

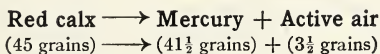
converted into the white powder. Lavoisier concluded that the "calx" of tin was formed by the combination of the metal with an active part of the air. He was then anxious to procure in a free state "the air" he assumed present in the calx. About this time, Priestley who was visiting Paris told Lavoisier of his experiments with the "calx of mercury" which could not only be prepared in the same way as the calx of tin, but could also be decomposed by further heating. Lavoisier heated four ounces of mercury in a retort, the neck of which was bent to pass up into a bell-jar inverted over mercury (Fig. 3.6). After twelve days of heating, the air in the retort and bell-jar diminished 8 cubic inches in volume, and 45 grains of mercury calx (mercuric oxide) had been produced. Furthermore, when a lighted candle was placed in the gas that remained in the retort and bell-jar it was immediately extinguished. The 45 grains of calx, strongly heated in a



Fisher Scientific Company

Fig. 3.4. These very old balances date at least to A.D. 79. They were found in the ruins of Pompeii.

smaller retort, decomposed, producing $41\frac{1}{2}$ grains of mercury and 8 cubic inches of Priestley's gas weighing $3\frac{1}{2}$ grains. Thus all of the air that had been "absorbed" by the mercury when it was heated in air was recovered in a pure state when the calx was heated.



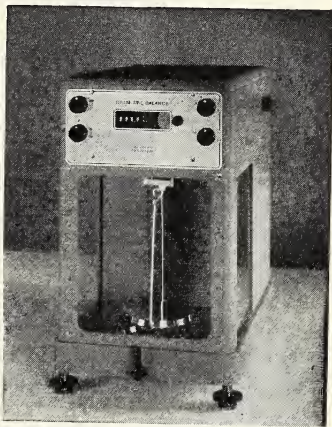
These findings are briefly enumerated below:

When mercury is heated in air: (1) the product formed is heavier than the original mercury; (2) something from the air united with the mercury; and (3) the increase in the weight of the mercury is exactly equal to the weight of air consumed. In other experiments Lavoisier also proved that (4) substances other than mercury when burned in air behave exactly like mercury. From his experiments he inferred that all burning consisted in the joining of some part of the air with the burning substance.

Lavoisier called the active component of air **oxygen** and his theory the **oxygen theory of combustion**. His theory soon became established

as a chemical law because so much evidence accumulated to support it. Lavoisier's work sounded the death knell of the phlogiston theory. Of equal or even greater importance is the fact that the methods he introduced may be considered the basis of the scientific method of investigation:

1. He collected all the facts pertaining to a problem whether obtained from his own experiments or from those of fellow chemists.
2. He carefully examined all these facts.
3. He formulated a theory in an attempt to explain the facts.
4. He tested the theory by further experiments.
5. He formulated a law from the tested theory.



Fisher Scientific Company

Fig. 3.5. This modern balance will weigh to one-one hundred thousandth of a gram. Operated by electricity, weights are selected simply by turning knobs on the central panel.

6. He used the law in attempts to explain other similar situations. Although he did not discover a single new substance, Lavoisier is

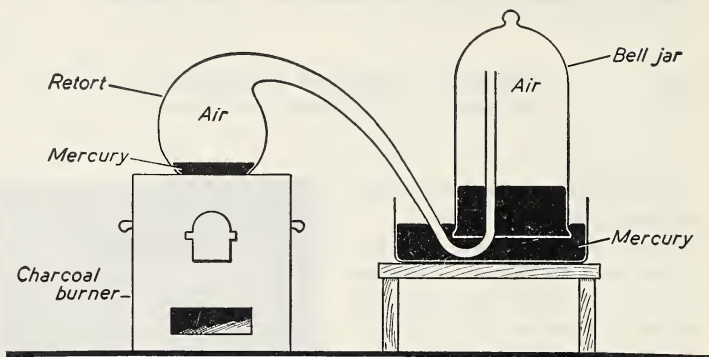


Fig. 3.6. A reproduction of a sketch made by Madame Lavoisier of the apparatus used by her husband in his famous experiments that led to the oxygen theory of combustion.

known as the “father of modern chemistry”. His investigations of chemical reactions, involving accurate weighings and calculations, made the Law of Conservation of Mass (see Chapter 9) a definite possession of chemists, and introduced a new era in chemistry.

It is ironical that a man who made the civilized world his debtor should have lost his head on the guillotine. At the time of his execution a fellow scientist wrote, “It required but a moment to cut off a head, the like of which one hundred years will not produce.”

EXERCISE

1. What was Johann Becher's explanation of the nature of ordinary burning (combustion)?
2. What is the phlogiston theory of combustion and by whom was it suggested?
3. Discuss an important difficulty that this theory could not satisfactorily explain. How did the phlogistonists attempt to explain it?
4. Why did the early investigators fail to find the true explanation of ordinary burning?
5. Describe Priestley's experiment with red mercuric oxide.

6. Why did Priestley give the name "dephlogisticated air" to the gas he obtained in his experiment?

7. Describe Lavoisier's experiment on the calcination of tin. What problem was suggested as a result of this experiment?

8. Describe Lavoisier's twofold experiment on the formation, and later, the decomposition of mercuric oxide. Illustrate your answer with a labelled drawing of the apparatus used.

9. Briefly enumerate four findings from Lavoisier's experiment that led him to formulate his "oxygen theory of combustion".

10. Lavoisier is commonly credited with being "the father of chemistry". The famous German scientist Liebig said: "Lavoisier discovered no new body, and no new property. His mortal glory consists in this — he infused into the body of science a new spirit. His work was to interpret the discoveries of those who had gone before him in the light of quantitative measurements". (a) Explain in your own words Liebig's statement about Lavoisier. (b) Give the six steps Lavoisier considered essential in the scientific method of investigation.

11. Consult an encyclopaedia, or other library sources, and prepare a brief biographical sketch, suitable for a class report, of Lavoisier.

CHAPTER 4

Oxygen: The Most Abundant Element

On the 1st of August, 1774, I endeavoured to extract *air* from *mercurius calcinatus per se*, and I presently found that, by means of a lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it and found that it was not imbibed by it. But what surprised me more than I can well express was that a candle burned in this air with a remarkable brilliant flame.

JOSEPH PRIESTLEY

Oxygen was probably first prepared by the Swedish chemist, Karl Scheele, who decomposed nitric acid vapour, as well as saltpetre, by the application of heat. Scheele did not publish his results, so the credit for first preparation is usually given to Priestley whose method of preparation and collection has already been described. In addition



Fig. 4.1. Joseph Priestley (1733-1804).

to the experiments mentioned at the beginning of this chapter, Priestley studied the effects of oxygen, first on mice and later on himself, and was impressed by the exhilarating effects produced. "Who can tell," he wrote, "but that in time this pure air may become a fashionable article in luxury? Hitherto, only mice and myself have had the privilege of breathing it."

The study of oxygen is of major importance to both the professional chemist and the beginner. This importance depends upon a number of things, chief of which is the abundance of the element itself; the large number of compounds of which it forms a part; and the fact that the discovery of this element marked the beginning of modern chemistry.

Occurrence. Oxygen is the most abundant of the earth's elements. By weight it makes up nearly half our globe, including earth, ocean,

and air. It forms about one-fifth by volume of the atmosphere, eight-ninths by weight of all the water on the earth, and nearly half by weight of the materials in the earth's crust. Even the human body is

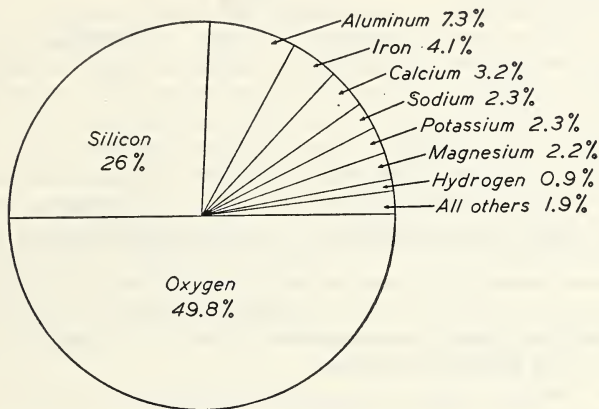
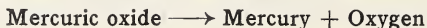


Fig. 4.2. Relative quantities of the elements in the earth. Oxygen makes up nearly half of our globe.

three-fifths oxygen by weight, and all animal and plant bodies contain a very high percentage of this element. Oxygen also plays an important part in the manufacture of synthetic products.

Preparation. Because oxygen is so plentiful, it might be assumed that it would be a simple matter to select one, or a mixture, of its many compounds as a source for preparing it in a pure form. In making such a choice, three important factors should be considered. Is the material cheap? Has it a high percentage of oxygen? Does it readily yield its oxygen? Air, sand, mercuric oxide, and potassium chlorate might be considered. Air is cheap and plentiful, but the separation of oxygen from the other gases with which it is mixed in air is a difficult matter requiring expensive equipment (p. 37). Sand is very rich in oxygen, but cannot be persuaded to part with it even when heated to extremely high temperatures. When mercuric oxide is heated in a hard-glass test-tube and the gas produced is tested with a glowing splint, the splint promptly bursts into a full and brilliant flame, and mercury, in the form of silvery beads, gathers on the sides of the tube. But mercuric oxide is expensive, has a low percentage of oxygen, and therefore is not a suitable source of oxygen. However, the simplicity of the chemical change involved may well attract our

attention. This change can be represented by the following word equation:



Potassium chlorate is much cheaper than mercuric oxide, and when heated yields a greater proportion of oxygen. This substance is convenient, inexpensive, and suitable for preparing oxygen in sufficient volume for laboratory study. Potassium chlorate is a white solid composed of three elements, potassium, chlorine, and oxygen. If crystals of it are placed in a hard-glass test-tube and heated, they release oxygen rather reluctantly, and only after being strongly heated. The potassium chlorate first crackles loudly, or **decrepitates**, then it melts. Finally, vigorous bubbling occurs in the molten liquid. A glowing splint test indicates that the escaping gas is oxygen. As the heating process is continued, it is noticed that the bubbles finally stop forming and suddenly the molten mass becomes and remains a white solid. This solid has different properties from the original potassium chlorate and is called **potassium chloride**.

The chemical change occurring can be represented by the following equation:

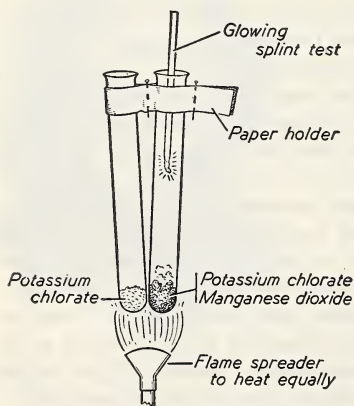


Fig. 4.3. Catalysis. When potassium chlorate and a mixture of potassium chlorate and manganese dioxide are heated under the same conditions, oxygen is given off more rapidly from the mixture than from the potassium chlorate alone.

Catalysis and catalysts. If some potassium chlorate is heated until it *just melts* and a glowing splint is placed in the upper portion of the test-tube, it is found that no oxygen is produced. If now, however, the flame is removed and a small pinch of a black powder called **manganese dioxide** is dropped into the tube, a rapid evolution of gas is observed, and if the glowing splint test is repeated the splint bursts into flame, showing that oxygen is being produced at a relatively low temperature.

Again, if two test-tubes, one containing a mixture of manganese dioxide and potassium chlorate, and the other an equal quantity of potassium chlorate only, are

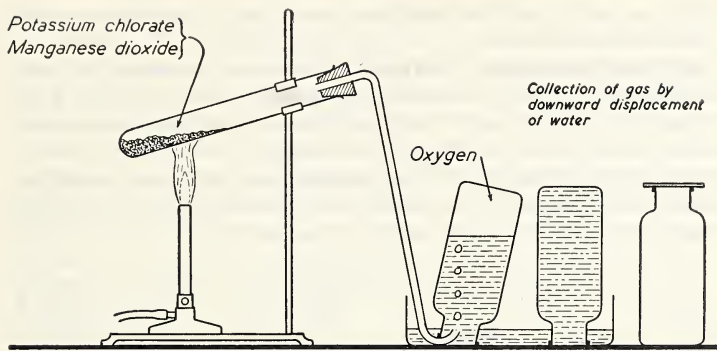


Fig. 4.4. The laboratory preparation and collection of oxygen.

placed in a common holder and heated under the same conditions for the same length of time, oxygen will ultimately be given off by both tubes. The tube containing the manganese dioxide, however, bubbles more briskly than the tube with potassium chlorate only. A glowing splint test on both tubes indicates that oxygen is being produced at a much faster rate in the tube containing the mixture.

If the residue from the tube which contained the mixture of manganese dioxide and potassium chlorate is now thoroughly washed with boiling water, filtered, and dried, a black residue, resembling manganese dioxide, remains on the filter paper. When this residue is added to a fresh quantity of melted potassium chlorate, it acts exactly as did the manganese dioxide in the first experiment. It can also be shown that this residue is equal in weight to the original manganese dioxide. Thus the manganese dioxide caused the potassium chlorate to yield its oxygen at a faster rate and at a lower temperature, but itself remained unchanged. It is said to be a **catalyst** in this reaction, and the action is called **catalysis**. *A catalyst is a substance used to alter the rate of chemical reaction without undergoing any permanent chemical change.* Catalysts do not always “speed up” a reaction. The label on a bottle of hydrogen peroxide often reads, “contains acetanilide”. The acetanilide has been added to keep the peroxide from decomposing too rapidly. Substances that increase the rate of a chemical

reaction are called **positive catalysts**; those that retard the rate are called **negative catalysts**.

Laboratory preparation of oxygen. If a mixture of potassium chlorate and manganese dioxide is heated in a hard-glass test-tube (Fig. 4.4), the oxygen can be collected easily by the downward displacement of water. Several bottles of the gas thus collected can be used to study the properties of oxygen. Priestley's experiments with gases which he called "airs" resulted in his invention of the well-known pneumatic trough, essentially the same as that in use today.

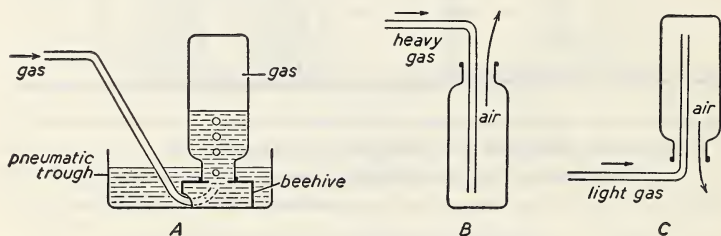


Fig. 4.5. Three methods of collecting a gas. *A*, downward displacement of water. *B*, upward displacement of air. *C*, downward displacement of air.

Some additional methods of preparation. Oxygen can be liberated from some of its compounds without being heated. If water is added to sodium peroxide, oxygen is liberated very rapidly. A commercial product called "oxone" is essentially sodium peroxide and is sold for use in a special generator. Oxygen can be prepared from water by the use of electrical energy, but the chief commercial source is liquid air.

Physical properties. As might be deduced from its presence in the atmosphere, oxygen is a colorless, odorless, and tasteless gas. It is slightly soluble in water, about 3 volumes dissolving in 100 volumes of water at room temperature, and nearly 5 volumes in 100 volumes of ice water. Hence, cold water saturated with oxygen will give off bubbles of oxygen if allowed to stand in a warm room. Oxygen is 1.105 times as dense as air. It can be liquefied by cooling to -119°C . under a pressure of 50 atmospheres. Liquid oxygen has a slightly bluish colour and boils at -182.97°C . at atmospheric pressure. When cooled to -218.4°C ., it freezes to a pale-blue snow-like solid.

Chemical properties. Because oxygen occurs in so many substances, it might be concluded that it is a very active element. When exposed for a long time to air, iron rusts, wood rots, animal remains decay, and many other similar changes, resulting from the slow action of

oxygen, take place. A freshly-scraped piece of iron soon becomes dull and tarnished. The oxygen of the air slowly unites with the iron to form a new substance called **iron oxide** (ferric oxide). Similarly, the oxygen in the air we breathe slowly reacts with digested food to form carbon dioxide and to release the energy necessary to activate and keep the body warm. *The process by which oxygen combines with some other substance is called oxidation.* When this action is slow and without perceptible heat, as when iron rusts, it is called **slow oxidation**. When **rapid oxidation** occurs, e.g., when wood burns, noticeable heat and light are produced, and the process of burning is known as **combustion**. Although oxygen supports combustion, it does not itself burn.

Combustion. The term combustion, although most commonly used with reference to oxygen, sometimes includes chemical reactions in which oxygen is not involved (e.g. hydrogen and antimony will burn in chlorine gas and produce heat and light). *Combustion is any chemical reaction in which noticeable heat and light are produced.* It should be noted that although heat is produced during slow oxidation, it is given off so slowly it cannot be easily detected. All chemical reactions that give off heat are called **exothermic reactions**; hence all oxidations are exothermic.

Reactions that absorb heat are called **endothermic reactions**. For example, the decomposition of mercuric oxide into mercury and oxygen requires heat; if the supply of heat is interrupted, the reaction ceases. Hence this reaction is endothermic.

Kindling temperatures. Some substances, apparently inactive with oxygen at ordinary temperatures, become quite active at higher temperatures. Wood, sulphur, coal, and other substances combine slowly with oxygen at ordinary temperatures, but the reaction may be so slow that only careful study over a long period of time indicates any perceptible change. If, however, the temperature is raised, the speed of the reaction increases and finally actual combustion may begin.

The oxidation of phosphorus, an exothermic reaction, occurs so

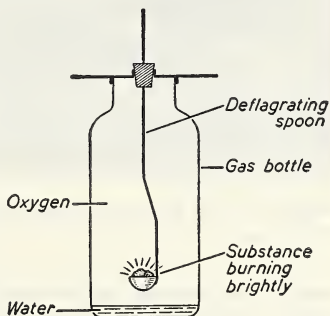


Fig. 4.6. Combustion in oxygen using a deflagrating spoon. The resulting oxide is shaken with water and the solution tested with an indicator.



U.S. Bureau of Mines

Fig. 4.7. Coal dust and air form an explosive mixture. Photograph of a controlled experiment carried out by the United States Bureau of Mines.

rapidly even at room temperature that it is likely to ignite "spontaneously". Sulphur must be heated to a higher temperature than phosphorus, and coal to a still higher temperature before combustion begins. The lowest temperature at which a material will ignite, or start burning, is called its **ignition** or **kindling temperature**. In starting a coal fire, we apply our knowledge of kindling temperatures by so arranging the paper, shavings, and larger pieces of wood and coal that, as each material ignites, the next in order is raised to a temperature at which rapid oxidation occurs.

Spontaneous combustion. If a small piece of yellow phosphorus is dissolved in carbon disulphide and the solution poured on a piece of filter paper and exposed to air, the carbon disulphide evaporates rapidly and minute pieces of phosphorus are left on the paper. Slow oxidation occurs in the finely-divided pieces of phosphorus so rapidly that the phosphorus ignites in about two minutes. Whenever a substance undergoing slow oxidation does not readily conduct heat, or when the material is so enclosed that free circulation of air around

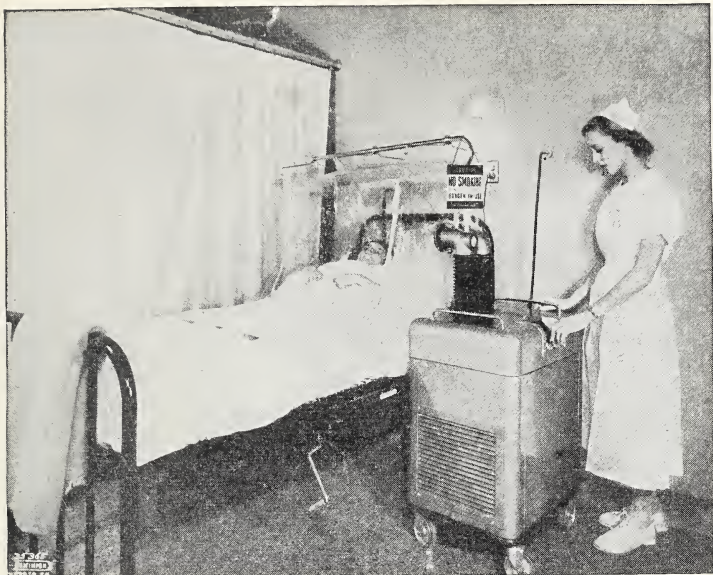
*Canadian Liquid Air*

Fig. 4.8. A patient undergoing treatment in an oxygen tent. In modern hospitals oxygen is piped to each room.

the material is impossible, the heat due to the oxidation accumulates and, if the ignition temperature of the material is low enough, **spontaneous combustion** results. Paints containing linseed oil “dry” because of oxidation. If rags, soaked with paint or linseed oil, are thrown in a heap, there may be little chance for air circulation and the accumulating heat may soon raise the temperature of the oil to its ignition point and spontaneous combustion results. Many serious fires originate in this way. Spontaneous combustion may occur in huge piles of coal, or in poorly ventilated coal mines. Poorly cured, moist hay will ferment with a resultant production of heat. If this heat does not escape, the hay reaches its ignition temperature and a fire results.

A test for oxygen. To distinguish one substance from all other substances, chemists make use of certain characteristic properties. For example, carbon dioxide is the only gas that will turn limewater milky. Hence, if a gas is bubbled into limewater and a white precipitate results, the gas is undoubtedly carbon dioxide. Although oxygen is not the only gas capable of rekindling a glowing splint, it is the only

common one, and this test is usually considered sufficient to identify oxygen. However, nitrous oxide, a gas commonly used by dentists as an anaesthetic (p. 255), will also rekindle a glowing splint. Consequently, a glowing splint is merely an "indication" of oxygen and a "conclusive test" is made by adding the gas to a water solution of pyrogallic acid and potassium hydroxide. Oxygen dissolves readily in this mixture, and at the same time turns the colorless solution to a deep brown colour. No other gas will behave in a similar manner.

Oxides. Sulphur, carbon, phosphorus, sodium, magnesium, calcium, and iron burn vigorously in pure oxygen. Whenever oxygen combines

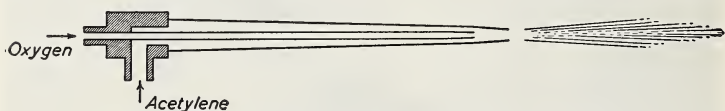


Fig. 4.9. A simplified diagram of an oxy-acetylene torch.

with another element, the resultant compound is called an **oxide**. Oxides occur as gases, liquids, and solids. When the gas produced from burning sulphur, **sulphur dioxide**, is shaken with a small amount of water, the resulting solution turns blue litmus red; renders pink phenolphthalein colorless; and changes neutral (green) bromthymol blue solution to yellow. When magnesium is burned in oxygen, the product of the combustion is a white solid called **magnesium oxide**. When this is shaken in water, it partially dissolves, forming a solution that turns red litmus blue; colorless phenolphthalein pink or red; and the green, neutral solution of bromthymol blue to a blue colour. Substances like litmus, phenolphthalein and bromthymol blue are known as **indicators** because they indicate whether a solution to which they are added is an acid or a base.

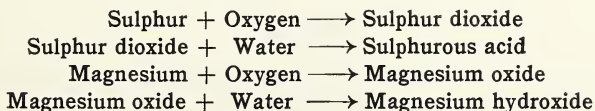
By the use of indicators, most oxides can be divided into two classes. Oxides of non-metals such as sulphur dioxide and carbon dioxide that combine with water to form acids are called **acidic oxides** or **acid anhydrides**. Oxides of metals such as sodium oxide and magnesium oxide, that combine with water to form bases are called **basic oxides** or **basic anhydrides**. Other oxides, e.g. copper oxide, that do not react with water are called **neutral oxides**. When magnesium oxide is shaken with water, it first forms **magnesium hydroxide**, which in turn dissolves in the water present to yield a solution that is slippery to the touch, bitter in taste, and that produces the basic action on indicators previously mentioned. The acidic oxide, sulphur dioxide, reacts with

*Canadian Liquid Air*

Fig. 4.10. Using an oxy-acetylene flame for cutting metals.

water to form **sulphurous acid**, a solution of which is sour, or acrid, to the taste and has a different effect on indicators than has the base. The properties of these important substances called **acids** and **bases** will be discussed in Chapter 16.

The chemical reactions mentioned above are summarized by the following simple "word equations".



Uses. A study of the properties of any substance suggests possibilities for its commercial uses. Pure oxygen has many industrial applications.

Most of the oxygen prepared for industrial use is obtained from liquid air and is sold in steel cylinders. In medical practice, it is used to improve respiratory action in cases such as pneumonia, tuberculosis, infantile paralysis, or poisoning from carbon monoxide, or when the

oxygenation of the blood has been impeded, or the patient is dangerously weak. It is usually administered under an oxygen tent. In high



Canadian Liquid Air

Fig. 4.11. Using an oxy-acetylene flame for welding metals.

altitude flying and in submarines, where the natural supply of oxygen is limited, tanks of compressed oxygen are carried as standard equipment. Emergency supplies are also kept on hand in coal mines and at fire-fighting stations. Because oxygen is the only gas that will support life, it is always a component of any gas mixture used to produce anaesthesia. By far the largest amount of commercial oxygen used, however, is in the operation of oxy-acetylene torches employed in cutting and welding metals.

Pure oxygen is also used in photoflash lamps. Magnesium or aluminum foil is enclosed in a bulb

containing pure oxygen. When the bulb is inserted in an electric circuit and the current turned on, the metal burns brilliantly and almost instantaneously, thus providing a controlled source of light for "flash" photography.

Carbon, a non-metal, can be burned out of automobile cylinders by means of oxygen and in a few years it may be possible to employ commercial oxygen, instead of air, in blast furnaces where high temperatures are required.

EXERCISE

1. From what compound was oxygen first obtained and how was it liberated?
2. Discuss the occurrence of oxygen in nature.
3. In selecting a substance as a suitable source of oxygen, what three factors should be considered?
4. In the experiment illustrated by the accompanying diagram, mercuric oxide is being strongly heated in a test-tube. (a) Write a word equation for this reaction. (b) Give the colour and state the substances at 1 and at 3. Account for the formation of the substance seen at 3. (c) A glowing splint slowly lowered into the tube glows with brilliant whiteness at 4, but not more brilliantly at 2

than in air. Account for each observation. (d) As the splint is slowly raised to the mouth of the tube, it ceases to glow. Why? (e) As the test-tube cools, a reddish deposit gathers on the inside of the tube just below 3. Account for this.

5. (a) Give five observations noted when crystals of potassium chlorate are intensely heated in a hard-glass test-tube. (b) Write a word equation for this reaction.

6. (a) Describe the laboratory method of preparing and collecting oxygen. (b) Make a labelled diagram of the apparatus used and include a word equation for the reaction.

7. (a) What is a catalyst? (b) Describe an experiment to prove that manganese dioxide acts as a catalyst in the preparation of oxygen from potassium chlorate.

8. (a) List seven physical properties of oxygen. (b) What is the outstanding chemical property of oxygen?

9. (a) Define, using examples: oxidation; slow oxidation; burning (combustion). (b) Give an example of combustion without the presence of oxygen.

10. Distinguish between exothermic and endothermic reactions. Give an example of each.

11. (a) Criticize the statement, "The ignition temperature is the temperature at which a substance will burn". (b) Give a correct definition of ignition temperature. (c) Explain the successive use of paper, kindling wood, and finally coal in starting a coal fire in a furnace.

12. (a) Explain the cause of spontaneous combustion. (b) List four examples of locations where fires often break out spontaneously. (c) Suggest safety precautions for preventing spontaneous combustion.

13. (a) Why is a glowing splint test not a conclusive test for oxygen gas? (b) By what conclusive test can oxygen be distinguished from all other gases?

14. (a) What is a chemical indicator? (b) Name three indicators and state their colours in both acids and bases.

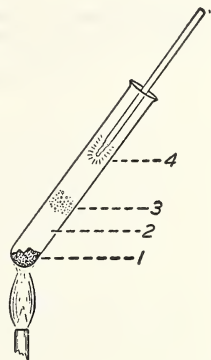
15. Define, giving an example in each case: oxide; acidic oxide (acid anhydride); basic oxide (basic anhydride).

16. (a) Name the products formed when the following chemical elements are separately burned in jars of oxygen: carbon; sulphur; phosphorus; mercury; magnesium; sodium; calcium; and iron. (b) Write word equations for each of these reactions. (c) Name the acid or base formed in each case when the oxides named in (a) are separately shaken with a small quantity of water. (d) Write word equations for each of the reactions in (c).

17. List the chief uses of commercial oxygen and name the physical and chemical properties upon which each use depends.

18. If 2.56 gm. of a metal combine with oxygen to form 2.88 gm. of the oxide of the metal, find the percentage of oxygen in the oxide.

19. A hard-glass test-tube was carefully weighed and a quantity of potassium chlorate was put into it. It was weighed again and then carefully heated until no more oxygen was evolved. The cooled test-tube containing potassium chloride was then weighed.



Weight of empty test-tube	18.00 gm.
Weight of tube + potassium chlorate	24.13 gm.
Weight of tube + potassium chloride	21.73 gm.

From this data, calculate (a) the percentage of oxygen in potassium chlorate,
(b) the percentage of potassium chloride.

CHAPTER 5

Nitrogen and the Atmosphere

The gas, nitrogen, serves as a blanket to keep the world from burning up in the oxygen of the atmosphere . . . [if the nitrogen of the air were replaced by oxygen] . . . The slightest fire could start a great and overwhelming conflagration. A single torch might commence the conflagration of the world.

HOLLIS GODFREY

In 1772, Dr. Rutherford of the University of Edinburgh demonstrated that if living animals were permitted to breathe within a confined volume of air, there was ultimately left only an inert and peculiar gas. This he called "phlogisticated air". About the same time, Priestley showed that after charcoal was burned in a confined volume of air, the gaseous material remaining was also phlogisticated air. Scheele first clearly pointed out that air is a mixture of two gases that he called *active air* and *inactive air*. Lavoisier recognized that inactive air was an element and named it *azote* from a Greek word meaning "without life". Later (1823), the name **nitrogen** was suggested because this element was found to be a constituent of nitre or saltpetre.

NITROGEN

Occurrence. About 78% of atmospheric air is free nitrogen. The presence of such a large amount dilutes the oxygen and slows down oxidation. Without this dilution, the combustion of fuels could not be controlled and most metals would corrode so rapidly that their use would be impracticable.

Nitrogen also occurs in combination in nature. Small amounts of potassium nitrate are present in most soils and there is a huge deposit of sodium nitrate in Chile and Peru. Nitrogen is also a constituent of many vegetable and animal substances.

Preparation. 1. *Atmospheric nitrogen.* Nitrogen is prepared from air by the removal of oxygen. This withdrawal is effected in two ways: one method takes advantage of the affinity various substances have for oxygen, and the other utilizes the differences in boiling points of the various components of liquid air.

(28:28.9) and can be liquefied and solidified if sufficiently cooled and compressed.

Chemical. Nitrogen neither burns nor supports combustion. A water solution has no effect on litmus. The chief characteristic of nitrogen is its **inertness**, but it does react with some of the most active metals at high temperatures. Nitrogen combines with oxygen only at very high temperatures (p. 252), and with hydrogen under special conditions (p. 249).

Uses. By far the largest use of nitrogen is in the synthesis of nitrogen compounds. These reactions are discussed under "nitrogen fixation" in Chapter 24.

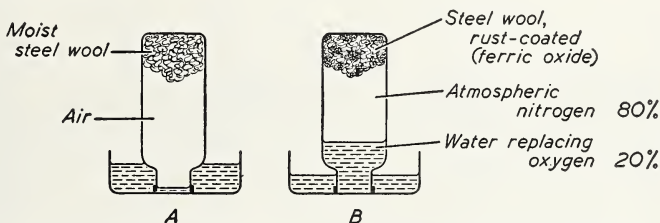


Fig. 5.2. Experiment with steel wool to determine the proportions by volume of oxygen and nitrogen in the atmosphere. *A*, before oxidation of the iron has started. *B*, after oxidation has ceased.

Because of its inertness, nitrogen is used to fill electric lamps as its presence prevents combustion and retards the vaporizing of the hot tungsten filament.

THE ATMOSPHERE

The term **atmosphere** is given to the mixture of gases that surrounds the earth. Until recent times it was thought that the atmosphere was about one hundred miles high, but with the discovery of radar, Geiger counters, and V-2 rockets we are learning that this "ocean of air" is over two thousand miles deep and of great complexity. The atmosphere consists of three shells. The lower **troposphere** is about ten miles deep; the **stratosphere** extends from the top of the troposphere to a height of approximately fifty miles, and the **ionosphere** rises to a height of more than two thousand miles. The troposphere, although consisting of less than one-third of 1% of the total volume of the atmosphere accounts for more than 79% of the total mass of air.

The following account refers to the characteristics of air near the earth's surface, i.e. in the lower level of the troposphere.



International News

Fig. 5.3. A V-2 rocket is launched. Such rockets carry recording instruments and are used to explore the upper atmosphere. They have reached heights in excess of ninety miles.

Properties. Air is a mixture of various gases and as such exhibits the properties of each component. At 0°C . and 760 mm. pressure a litre of air weighs 1.29 grams. Because of its great height, the atmosphere exerts a considerable pressure at sea level (Chapter 10). This pressure decreases from 760 mm. at sea level to about 40 mm. at ten miles and about 0.1 mm. at thirty miles.

Composition. The principal components of air are the two gases, oxygen and nitrogen. Oxygen makes up approximately one-fifth, and nitrogen four-fifths, of the whole. In addition to these principal substances, however, certain others are always present. The percentages of the various components vary with the altitude. The following table shows the average composition by volume of dry air at sea level.

The proportions of oxygen and carbon dioxide in a given locality may fluctuate because of variations in respiration, combustion, and photosynthesis, but the action of winds and diffusion soon mix the altered air with the general mass of the atmosphere so that the variations in the composition of air at different localities are very slight.

COMPOSITION OF AIR

COMPONENT	PERCENTAGE {By Volume}
Nitrogen.....	78.03
Oxygen.....	20.99
Argon.....	.94
Carbon dioxide.....	.035
Helium.....	.0004
Neon.....	.0012
Krypton, Xenon.....	traces

Water vapour and dust are always present in air and are the only substances varying widely in percentages. The percentages of the components of air in the above table are determined on the assumption that the air is absolutely dry, and this is a condition never found in nature.

LIQUID AIR

Air was first prepared in the liquid state in 1877. Liquid air, however, could not be produced in large quantities until 1901 when a Canadian, E. A. LeSueur, perfected an apparatus at Sault Ste. Marie for such production. Today the manufacture of liquid air is an important industry, and is carried on in nearly every large industrial centre.

Preparation. After water vapour and carbon dioxide are removed from air, it is compressed under a pressure of about 100 atmospheres, i.e., of about 1500 lb. per sq. inch. The heat produced by this compression raises the temperature of the air. This heat is removed by cold water circulating through a coiled pipe in a condenser. The cold compressed air then goes to a liquefier consisting of a long, coiled copper tube. A needle valve at the lower end of the tube allows the air to expand rapidly. This expansion further cools the air that is returned to the compressor and the process is repeated. Each quantity of air escaping from the valve is colder than its predecessor until eventually the air is cooled below its liquefaction temperature, when it condenses.

Properties. Liquid air is a pale-blue liquid with a density slightly less than that of water. The boiling point varies between -195°C . and -185°C . Liquid air is kept insulated from external heat in double-walled flasks resembling thermos bottles (Dewar flasks). Since liquid air is extremely cold, many interesting experiments can be performed with it. A piece of rubber tubing, when immersed in liquid

air, becomes as brittle as glass; flowers, vegetables, and fruits become so hard and brittle that they shatter to pieces if dropped; and mercury is frozen hard enough to be used as a hammer to drive nails.

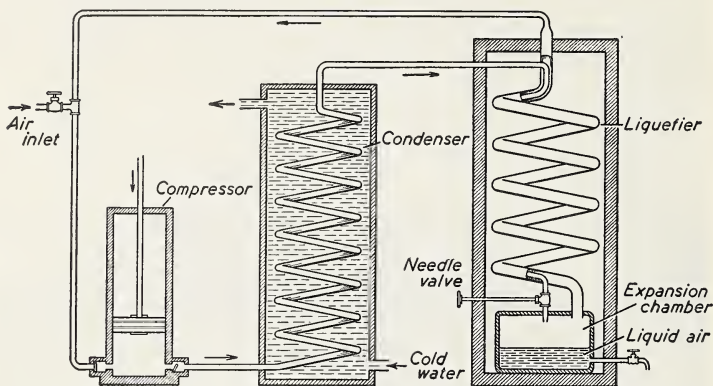


Fig. 5.4. A simplified diagram illustrating the method used to liquefy air.

Uses. Liquid air is used as a source of oxygen, nitrogen, argon, and neon. Because liquid air is a mixture and not a compound (Chapter 9), the various liquid components boil off at different temperatures. Kept in an open vessel, it becomes richer in oxygen because nitrogen boils at a lower temperature than oxygen. The various components of liquid air are separated by using a fractionating column not unlike that used for distilling petroleum.

INERT GASES

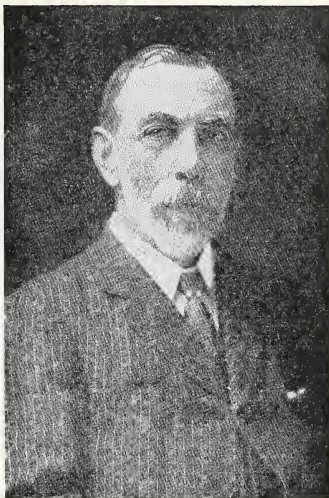
An account of the discovery and investigation of the inert gases in the atmosphere reads something like a detective story. In 1892, Lord Rayleigh showed that a litre of nitrogen prepared by removing oxygen from air weighs 1.2572 gm., whereas a litre of nitrogen prepared chemically weighs 1.2506 gm. This indicated that when nitrogen was prepared from the atmosphere some substance denser than nitrogen remained. The problem then was to separate nitrogen from the unknown gas. Several methods of removing nitrogen from samples of "atmospheric nitrogen" were developed by Lord Rayleigh and Sir William Ramsay. In one of these experiments, atmospheric nitrogen was passed over heated magnesium that combined with the nitrogen. A small volume of gas remained and this would not combine with the

magnesium. The experimenters were unable to make this gas enter into chemical combination with any other substance, so they gave it the name **argon**, meaning inactive. Later, suspecting impurities in this gas, they made efforts to purify it. The gas was liquefied by using liquid air as a cooling agent. When this liquid was vaporized and fractionated, it was found to contain minute amounts of four other inert gases. Three of these gases were new elements and were named **neon** (new), **xenon** (a stranger), and **krypton** (hidden). The fourth gas, **helium**, had been discovered previously.

Argon. Argon was the first of the inert gases found in the atmosphere. It constitutes about 0.94% by volume of the air and is produced from liquid air by fractionation. It is more efficient than nitrogen in gas-filled tungsten-filament electric lamps.

Neon. Neon, also produced from liquid air, is used in making "neon" advertising signs. When placed under low pressure in a glass tube and subjected to a high tension electrical discharge, neon produces a bright-red glow. Mixed with other gases in variously coloured glass tubes, neon produces many attractive contrasting colour effects (e.g. neon and mercury vapour in a yellow tube give bright green).

Helium. The name "helium" is derived from the Greek *helios* (the sun), because the element was first detected in the atmosphere of the sun. When a spectroscope was trained on the sun during an eclipse in 1868, a bright yellow line was observed in the spectrum. No substance previously discovered on the earth showed this same line in the spectrum. In 1895, Ramsay isolated a gas from an ore of uranium and in the spectrum of this gas he found a line corresponding to that observed in 1868 and gave the name helium to the new element. Unlike the other inert gases, helium is not prepared from air. Natural gases in Texas, Oklahoma, Ohio, and Kansas contain as much as 2.5% by volume of this element, which is now obtained commercially from



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Fig. 5.5. Sir William Ramsay (1852-1916), who with Lord Rayleigh discovered argon, and subsequently the other inert gases in the atmosphere.

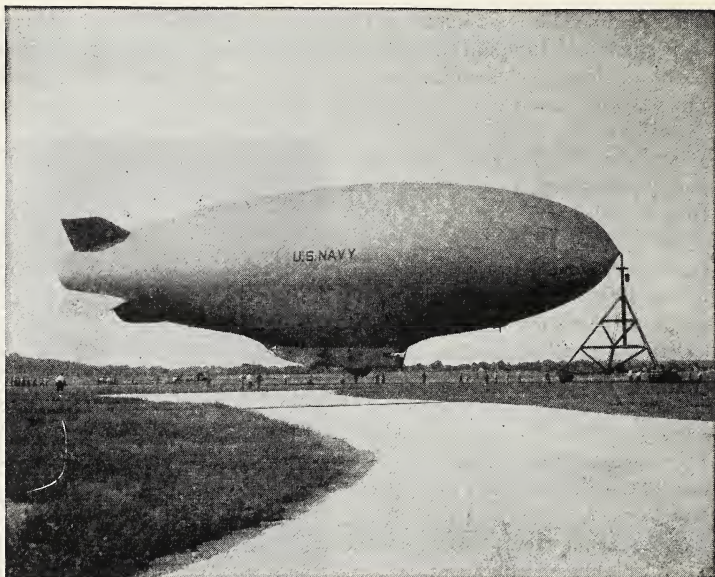
*Goodyear Tire and Rubber*

Fig. 5.6. This dirigible contains 975,000 cubic feet of helium.

these sources. Helium is the second lightest substance known and has 92% of the lifting power of hydrogen. This quality of lightness, coupled with its non-combustibility, renders it valuable in lighter-than-air aircraft. Since helium is less soluble in blood than nitrogen, a helium-oxygen mixture is supplied to deep-sea divers instead of compressed air. Under pressure, the nitrogen of the air dissolves in the blood and, when the pressure is released, the escaping nitrogen blocks the capillaries, causing serious effects and even death.

Krypton and xenon. Until recently krypton and xenon have not been produced in sufficient quantities to make their use practicable. A process recently patented in France, however, may result in greater use of these rare gases in the future. Light emitted from high-tension krypton and xenon tubes is very rich in infra-red and ultra-violet rays. Use of these lamps in radiology and health treatments promises to be valuable. Tiny lamps have been constructed for use in the cavities of the human body and these may be of great service in medical work.

EXERCISE

1. What researches led to the discovery of nitrogen?
2. Why and by whom was nitrogen named azote? What is the significance of its present name?
3. What is the importance of nitrogen in the atmosphere?
4. Write a note on the occurrence of nitrogen.
5. Describe the preparation of atmospheric nitrogen using yellow phosphorus. Make a labelled drawing of the apparatus used and write word equations for the reactions involved.
6. How does the nitrogen prepared in the above experiment differ from pure nitrogen extracted from a nitrate?
7. In preparing atmospheric nitrogen from the air of the laboratory, why not use a lighted splint, or burning candle for removing the oxygen rather than phosphorus?
8. Describe an experiment using moistened steel wool to determine the proportions, by volume, of oxygen and nitrogen present in the air. Make a labelled diagram of the apparatus used, and write a word equation for the reaction involved.
9. How is nitrogen prepared commercially? What property makes its separation possible?
10. How may pure nitrogen be prepared in the laboratory? Write a word equation for the reaction involved.
11. Tabulate seven physical and five chemical properties of nitrogen.
12. What are the commercial uses of nitrogen?
13. Distinguish between the troposphere, the stratosphere, the ionosphere, and the atmosphere.
14. (a) List the names and approximate percentages by volume of the different components present in dry air at sea level. (b) What other components are always present, but in variable amounts?
15. (a) Describe the liquefaction of air. (b) List some of the properties of liquid air.
16. (a) What clues and research led to the discovery of argon? (b) How is it prepared commercially? (c) What is the significance of the name argon?
17. (a) What was unique about the discovery of helium? (b) How is it prepared commercially? (c) What are the commercial uses of helium? (d) On what properties do these uses depend?
18. Give one commercial use for each of: argon; neon; krypton; xenon.
19. "Air is a mixture." Give two reasons for the belief that the oxygen and nitrogen in the atmosphere are not chemically combined.
20. In an experiment in which dry air was passed over heated copper, the unchanged nitrogen was collected in an evacuated flask. The weight of the nitrogen collected was found to be 18.559 grams and the oxygen with which it had been mixed caused the copper to increase in weight by 5.52 grams. From this data calculate the percentage by weight of the oxygen and nitrogen present in air.

CHAPTER 6

Hydrogen: Lightest of all Elements

By placing a saucer of white porcelain in a jet of inflammable gas burning tranquilly at an orifice, I found that the part of the saucer which the flame licked was moistened by small drops of liquid as clear as water, and which, in fact, appeared to be nothing but pure water.

MACQUER

The first mention of a gas evolved by the action of dilute acids on certain metals was made by Paracelsus (1493-1541). He observed that when iron and dilute sulphuric acid interact "an air arises which bursts forth like the wind". It was not until 1766 that an English scientist, Henry Cavendish, first obtained hydrogen in a pure state, described its true properties, and characterized it as a definite chemical element. He called this gas "inflammable air". A little later (1781), he proved that water was the only product resulting from the combustion of "inflammable air". Lavoisier (1783) renamed the gas hydrogen, a name derived from the Greek words that mean "water producer".

Occurrence. Although uncombined hydrogen is widely distributed in nature, it is not so abundant as oxygen. Mixed with other gases, free hydrogen is present in certain varieties of natural gas and in the gases that escape from volcanoes and petroleum wells. Mere traces are present in our immediate atmosphere but enormous quantities exist in the atmosphere of the sun and of many stars. The manufactured gas used for illuminating and heating purposes has a high content of free hydrogen.

Combined hydrogen is very abundant. It forms one-ninth (by weight) of its oxide, water. It is an essential constituent of all acids. Combined with carbon, it forms the hydrocarbons that make up petroleum and natural gas. In combination with carbon and oxygen it forms carbohydrates and fats, which are important substances in foods, as well as such



Fisher Scientific Company

Fig. 6.1. Henry Cavendish (1731-1810). From a drawing by Alexander in the Print Room of the British Museum.

common substances as the paper on which this book is printed. Hydrogen is a constituent of all living organisms, and comprises about ten per cent of our body weight.

Preparation. Like oxygen, hydrogen is obtained from its compounds. In most cases, water and certain dilute acids are the sources, and the methods of preparation are of four main types:

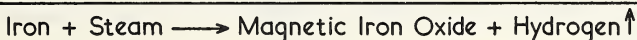
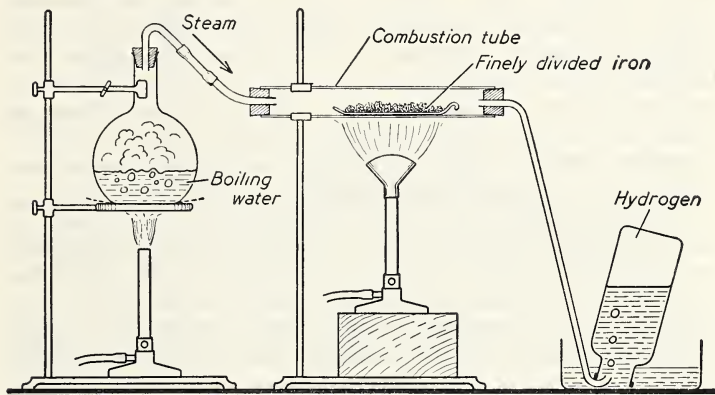


Fig. 6.2. Liberating hydrogen through the action of iron on steam. This is a cheap commercial source of hydrogen.

1. *The action of active metals on water.* The more active metals such as potassium, sodium, and calcium will displace hydrogen from cold water. The action with potassium and sodium, however, is so vigorous as to be extremely dangerous. This factor, coupled with the high cost of these metals, makes the method unsatisfactory for the commercial preparation of hydrogen.

Potassium and sodium are lighter than water and float on the surface. If a small piece of sodium is dropped upon cold water, it melts into a silvery globule that moves about rapidly on the water surface, liberating hydrogen with a hissing sound until it finally disappears. If the sodium is wrapped in a piece of lead foil pierced with a few holes and then dropped into water, the action proceeds smoothly and the gas evolved will displace the water from an inverted test-tube held over the rising bubbles. The collected hydrogen will give its characteristic "pop" or explosion when brought near a flame. The slippery

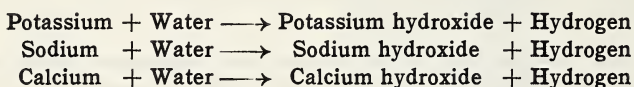
(soapy) feeling of the liquid remaining in the dish and its action on red litmus paper indicate the presence of a **base** or **hydroxide**.

When metallic potassium is dropped on the surface of water, the action is much more violent and so much heat is generated that the hydrogen evolved is ignited and burns; the flame is violet because of the presence of potassium vapour. In the case of the sodium, the heat generated is not usually sufficient to ignite the escaping hydrogen unless warm water is used or the globule is prevented from moving about on the surface of the water. The hydrogen then ignites, and because of the presence of sodium vapour burns with a yellow flame. Both experiments are dangerous and a glass plate should always be placed over the beaker to protect the experimenter's eyes.

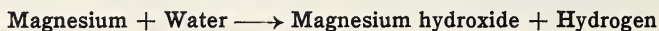
Metallic calcium, which sinks in water, acts rapidly but not violently, and the hydrogen is easily collected.

In all three cases, the metal used frees only half of the hydrogen in the water upon which it acts, and combines with the remaining half and all of the oxygen to produce the hydroxide of the metal. The hydroxides of potassium and sodium are readily soluble in the excess water, but can be recovered as white solids by evaporation of the remaining solutions. Calcium hydroxide (slaked lime) has a limited solubility and may be seen in suspended form in the water after the action.

The following word equations represent the chemical changes involved:



Less active metals, such as magnesium and iron, decompose water, but only at higher temperatures. Very finely divided magnesium decomposes cold water slowly, but reacts more rapidly with steam.



Iron also will liberate hydrogen from steam. If steam is passed through a tube containing finely divided red-hot iron, black magnetic oxide of iron is formed and hydrogen passes off as a gas. This method is used in the commercial preparation of hydrogen (Fig. 6.2).

2. Displacement of hydrogen from acids. If the hydrogen of water

can be replaced by certain metals, can the hydrogen of acids also be replaced by metals?

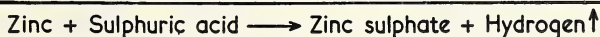
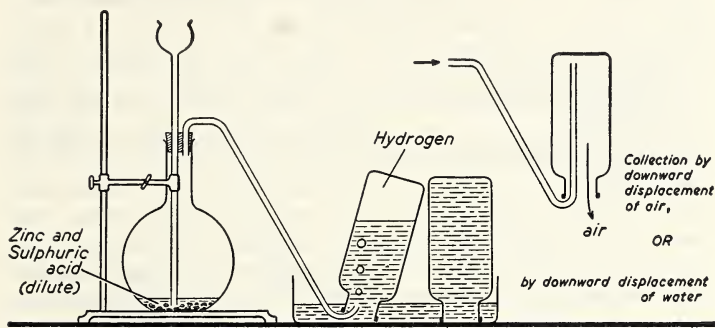


Fig. 6.3. The laboratory preparation and collection of hydrogen. Hydrogen may be collected by either the downward displacement of water or by the downward displacement of air.

ACTIVITY TABLE

Potassium
Sodium
Calcium
Magnesium
Aluminum
Zinc
Iron
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

The metals above hydrogen in the activity table (but none of those below it) will liberate hydrogen from dilute sulphuric acid or hydrochloric acid. The active metals at the top of the preceding list react violently; metals such as tin or lead, listed immediately above hydrogen, react so slowly as to be ineffective. The less active metals, located

below hydrogen in the list, do not form hydrogen if they interact with acids.

The metals most commonly used in the **laboratory preparation** of small quantities of hydrogen are zinc or iron, because the action, although rapid at ordinary temperatures, is not too violent and can be controlled easily.

A small handful of granulated zinc is placed in the flask (Fig. 6.3) and dilute sulphuric acid (or hydrochloric acid) is added through the thistle-tube until the lower end of the latter is covered. If pure zinc is used, the action is very slow, but it can be accelerated by adding some copper sulphate solution to the acid through the thistle-tube. Commercial zinc contains impurities (chiefly carbon), which accelerate the action without the addition of copper sulphate. The copper sulphate or the impurities in the zinc act as catalysts. Concentrated sulphuric acid, a dense, oily liquid, will not produce hydrogen unless it is diluted with water. The dilute acid may be prepared by slowly pouring the concentrated acid into five or six times the same volume of water. This should be done gradually and with constant stirring, since a great deal of heat is produced on mixing. Water should never be added to concentrated sulphuric acid (p. 206).

The action of this dilute acid on zinc proceeds smoothly, without heating, because the reaction is exothermic. Hydrogen is displaced from the acid and drives the air out of the flask. Since mixtures of hydrogen and air explode violently when ignited, flame should be kept away from the generator. The gas should be tested for purity by collecting it in an inverted test-tube (downward displacement of air) and testing it with a flame. A mixture explodes when brought to the flame, but the pure gas burns quietly. Since hydrogen is only very slightly soluble in water, it may be collected by the displacement of water once successive tests indicate that the pure gas is being evolved. Because the gas is lighter than air, the filled bottles should be kept in an inverted position.

The "word equation" for the interaction of the zinc and acid shows the production of a compound called **zinc sulphate**. The metal replaces the hydrogen of the acid, liberating it as a gas, and forms a soluble salt that remains dissolved in the excess water in the generator. If the solution is evaporated, transparent crystals of zinc sulphate are left.

The "activity table", discussed earlier, shows that any one of several metals might have been used instead of zinc. Magnesium and iron react vigorously with dilute sulphuric acid, producing hydrogen and a soluble salt of the metal in each case. Certain dilute acids, such as hydrochloric acid, can be used instead of sulphuric

acid. Nitric acid cannot be used because it is an active oxidizing agent (p. 252).

The following are typical "word equations":

Zinc + Hydrochloric acid (dilute) $\longrightarrow$ Zinc chloride + Hydrogen

**Magnesium + Sulphuric acid (dilute) $\longrightarrow$ Magnesium sulphate
+ Hydrogen**

**Aluminum + Hydrochloric acid (dilute) $\longrightarrow$ Aluminum chloride
+ Hydrogen**

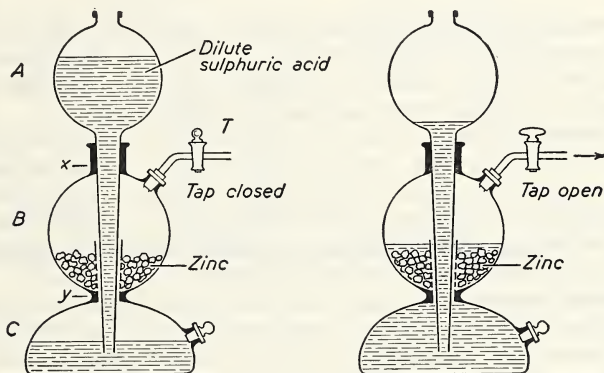


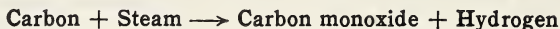
Fig. 6.4. A Kipp apparatus for generating gases.

Hydrogen may be kept "on tap" in the laboratory by the use of a Kipp apparatus. The top bulb (A) (Fig. 6.4) has a long stem extending almost to the base of the bottom bulb (C). It fits tightly at (X) and loosely at (Y). A supply of mossy zinc is placed in the middle bulb (B) and, with the tap open, dilute sulphuric acid is added through the top bulb until the lower bulb (C) is filled and the acid **covers** the zinc in the middle compartment.

This will supply a steady current of hydrogen, but if the **tap** is closed the effervescence continues for a short time, and the pressure created drives the acid down and away from the metal and up the long stem into the bulb (A) so that the action ceases. When a new supply of hydrogen is required, the action is ready to recommence the moment the tap (T) is opened. The escape of the stored gas permits the acid to run down the central stem. It rises into bulb (B) until it again floods

the zinc in the middle bulb, creating a new supply of hydrogen until the tap is closed once more. A Kipp may be used to generate other gases such as carbon dioxide and hydrogen sulphide.

3. *Action of a non-metal (carbon) on steam.* When steam is passed over a bed of white-hot coke (or anthracite coal), the carbon replaces the hydrogen of the steam to form carbon monoxide, and a mixture of this gas and hydrogen is produced.



The mixture of these two gases is called "water gas", and it is of great importance as an industrial fuel (p. 189). This "water gas" is one of the cheapest sources of industrial hydrogen, although the process of separating the two gases is a complicated one.

4. *Electrolysis of water.* When a direct current of electricity is passed through water containing a small amount of sulphuric acid, the water is broken down into the gases, hydrogen and oxygen, in the ratio of two volumes of hydrogen to one volume of oxygen. Where there is cheap electricity, this is another commercial method of preparing hydrogen, the details of which are discussed in the next chapter.

Physical properties. Hydrogen is a colorless gas that, in pure form, is tasteless and odorless. When commercial zinc and an acid are used in its preparation, the resultant gas has a distinct odour because of the presence of impurities which may be eliminated by passing the gas through solutions of sodium hydroxide and potassium permanganate. Hydrogen is only slightly soluble in water, less than 2 volumes of the gas dissolving in 100 volumes of water at 20° C. It is also the lightest known gas. One litre of pure hydrogen (measured at 0° C. and 760 mm. pressure) weighs only 0.08987 gm. (usually written 0.09 gm.), whereas one litre of air under the same conditions weighs 1.293 gm. Hydrogen is but one-sixteenth as dense as oxygen.

Hydrogen can be liquefied only with the greatest difficulty. Liquid hydrogen is colorless and boils at -253° C. When part of the liquid is allowed to evaporate rapidly, the remainder freezes to an ice-like solid, melting at -258° C. Exempting helium, all known gases solidify easily when placed in a vessel surrounded by liquid hydrogen.

Chemical properties. Pure hydrogen burns quietly in air with a pale-blue, almost colorless flame, but it is dangerously explosive if mixed with air or oxygen before ignition. Water is the only product of its combustion. The film of moisture often noticeable on the bottom of a vessel when first placed over a Bunsen flame or a lighted gas range,

is caused by the water produced when the hydrogen and hydrogen compounds in the illuminating gas burn.

One of the strangest truths of chemistry is illustrated by making use of a chemical property of hydrogen. Hydrogen, a highly inflammable gas, combines with oxygen, which supports combustion, to form water used to extinguish fire. Hydrogen, generated in a flask, is dried by passing it through a U-tube containing lumps of calcium

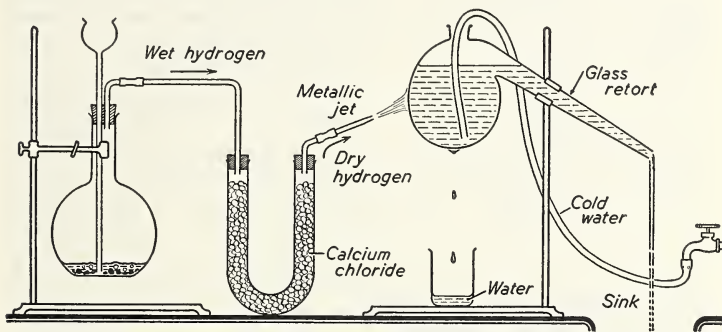


Fig. 6.5. When dry hydrogen is burned at a jet, water is the only product of combustion.

chloride, a substance that readily absorbs moisture. When the air, originally present in the flask, has all been displaced by the escaping hydrogen, the jet may be lit. This can be done safely by collecting the escaping gas in an inverted test-tube (downward displacement of air), carrying the tube mouth downwards to a flame at some distance from the apparatus, and then igniting the gas. Continue to collect and test the gas in this manner until it burns quietly and with no explosion. Then use this test-tube of burning hydrogen to ignite the escaping gas at the jet. If a glass jet is used, the flame has a yellowish tinge because of the sodium compounds in the glass, but if a metallic jet or a short piece of clay pipe-stem is substituted, a pale-blue, almost colorless, flame results. If this flame is allowed to strike against the surface of a glass retort, cooled by circulating water, the steam formed by the combustion of the hydrogen is condensed and visible drops of water trickle off the retort.

Although hydrogen itself burns, it will not support combustion. This is easily demonstrated by inserting a blazing splint into an inverted bottle of hydrogen. The hydrogen ignites with a "pop" and

continues to burn at the mouth of the bottle where it is in contact with the oxygen of the air, but the blazing splint inside the bottle is extinguished. If the splint is slowly withdrawn through the region of burning gas, it will be relighted by the almost invisible flame at the mouth of the bottle. A variation of this experiment is employed as a

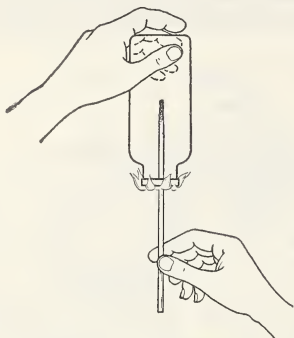


Fig. 6.6. Hydrogen burning quietly at the mouth of a bottle. When the blazing splint is inserted in the bottle, it is extinguished by hydrogen.

test for hydrogen. When a lighted splint, introduced into a bottle of gas, produces a sharp "pop" and an almost colorless flame that forms water as its only product, it may be assumed that this gas is hydrogen.

Because hydrogen has a strong affinity, or attraction for oxygen, it can remove oxygen from many metallic oxides. In Fig. 6.7, a current of dry hydrogen is being passed over red-hot black cupric oxide. A liquid that proves to be water collects in the cooler part of the tube and the black oxide changes to a reddish colour. The change in colour is brought about by the formation of a mixture of red (cuprous)

oxide and metallic copper. The ability of hydrogen to remove oxygen from a compound and to unite chemically with it makes hydrogen a **reducing agent**, and the chemical process is called **reduction**. Oxidation and reduction are opposite processes and reduction is always accompanied by oxidation, because if one substance is being reduced, another substance must be undergoing oxidation. In this experiment, the cupric oxide has been reduced to red cuprous oxide and metallic copper, while the hydrogen has been oxidized to form water. The cupric oxide acted as an "oxygen giver" and is called an **oxidizing agent**. The hydrogen acted as an "oxygen taker" (deoxidizer) and is called a **reducing agent**.

Hydrogen reduces the oxides of most of the heavier metals in a similar manner, but cannot reduce the oxides of the lighter metals, potassium, sodium, calcium, magnesium, and aluminum. There are other reducing agents more commercially useful than hydrogen. Carbon in the form of coal or coke is commonly used in industry (p. 170).

Hydrogen and chlorine combine gradually in diffused daylight, but unite explosively if exposed to direct sunlight, forming hydrogen

chloride gas. Hydrogen will also unite with molten sulphur to form hydrogen sulphide, and with nitrogen (under pressure and in the presence of catalysts) to form ammonia (p. 249).

Uses of hydrogen. Because of its extreme lightness, large quantities of hydrogen have long been used to inflate balloons and dirigibles, but the danger of fire or explosions from lightning and electrical sparks makes its use extremely dangerous, and the history of hydrogen-filled aircraft has had more than its share of tragedy. The United States possesses a larger supply of helium than any other nation, obtaining it by condensation from Texas and Oklahoma natural gases. While

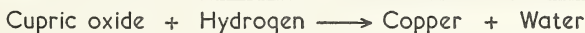
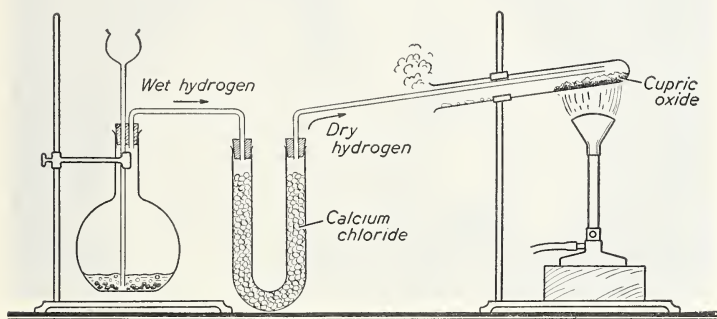


Fig. 6.7. The reducing action of hydrogen. When dry hydrogen is passed over heated cupric oxide, it removes oxygen from the compound forming water and leaving copper.

helium possesses only about 92% of the lifting power of the same volume of hydrogen, it is non-inflammable and is therefore preferred for use in airships. A law passed in 1938 placed its export under United States government control to prevent other nations from using helium for military purposes. Millions of pounds of cottonseed oil, coconut oil, and peanut oil are treated every year with hydrogen gas in the presence of finely divided nickel or nickel oxide, acting as catalysts. This process, called **hydrogenation**, converts these oils into fats that are solids or semi-solids at ordinary temperatures. Substitutes for lard are made from the chemical union of hydrogen with cottonseed oil. Butter substitutes such as margarine are also made in this way. Large quantities of fish oils, which were formerly almost useless, when hydrogenated can be used in the manufacture of soap.



Canadian General Electric

Fig. 6.8. A welder adjusting an atomic hydrogen torch. The temperature of the flame is approximately $4,000^{\circ}\text{C}$.

Hydrogen was formerly used to cut and weld metals in an oxy-hydrogen blowpipe, similar to the oxy-acetylene burner shown in Fig. 17.16. This type of burner was invented more than a hundred years ago and has been largely replaced by the hotter oxy-acetylene flame. The blast lamp often used in the laboratory to bend or work glass is a modification of the oxy-hydrogen blowpipe. Here, illuminating gas (containing hydrogen mixed with other gases) burns in a stream of compressed air with a much hotter flame than the Bunsen flame, the usual source of heat for chemical experiments. Recently, an extremely hot flame (about $4,000^{\circ}\text{C}$.) has been developed by an electric welding arc using "atomic hydrogen". In this invention, hydrogen gas is passed through an electric arc created between tungsten electrodes. This splits the hydrogen molecules into their atoms (see Chapter 11). On leaving the arc, the atoms combine again to form molecules and the heat, absorbed from the arc in order to break up the molecules, is now released and added to that produced by the burning of the hydrogen as it combines with the oxygen of air surrounding the arc.

Fuel gases such as water gas and illuminating gas that contain appreciable quantities of hydrogen are extremely useful for heating and lighting. When petroleum is refined, hydrogen is used to increase the yield of gasoline. England and Germany have plants that convert cheap grades of coal into gasoline and lubricating oils by using hydrogen under pressure as a part of the conversion process. Wood alcohol (methyl hydrate) can be made by heating wood in the absence of air, but large quantities of this product are now manufactured by the union of hydrogen with carbon monoxide gas in the presence of a suitable catalyst. Hydrogen can also be made to combine with the nitrogen of air, forming ammonia gas used in the manufacture of artificial fertilizers (p. 250). Hydrogen will also combine with chlorine in the manufacture of hydrochloric acid. While hydrogen has some laboratory use as a "reducing agent", in industry it is much cheaper and also more convenient to use coke or some other form of carbon.

EXERCISE

A

1. (a) By whom and when was hydrogen first prepared in a pure state? (b) What led the discoverer to call it "inflammable air"? (c) Give the origin and meaning of the name hydrogen.
2. Discuss the occurrence of hydrogen in nature under the headings (a) uncombined hydrogen, and (b) combined hydrogen.
3. (a) In obtaining hydrogen from its compounds, what are the two chief sources used? (b) List four general methods used in preparing hydrogen from the compounds named in (a).
4. A small piece of freshly-cut sodium becomes tarnished on exposure to air. When dropped on the surface of cold water, this irregular piece of sodium takes on a spherical shape. It appears to be at or slightly above the surface of the water. It moves rapidly along the surface of the water tracing a zig-zag path and produces a hissing sound as it moves. A white cloud is seen in the air immediately above the moving sphere. A white solid which settles into the water and disappears is also seen below the sphere. No flame is normally seen, but if the sodium sticks to the side of the containing vessel and remains in one spot, a yellow flame is commonly seen. The sodium sphere becomes smaller and finally disappears. (a) Explain the cause of each of these phenomena. (b) Write word equations for any two chemical reactions that occur in this experiment.
5. (a) In the reaction between potassium and water explain why (i) the potassium floats, (ii) the metal melts, (iii) the hydrogen produced burns without the application of a flame, (iv) the flame has a lilac colour, (v) the resulting solution is slippery to the touch. (b) Write a word equation for the action of potassium on water.
6. Briefly describe a method for collecting and identifying the hydrogen evolved when sodium is allowed to react with water.

7. (a) List four observations noted when a piece of metallic calcium is dropped on the surface of cold water in a beaker. (b) Write a word equation for the reaction in (a). (c) Give two reasons why the action of the metals potassium, sodium, and calcium, on water, is not regarded as a satisfactory method for the laboratory preparation in quantity of hydrogen.

8. Write word equations for: (a) The action of hot water on finely-divided magnesium. (b) The action of steam on highly-heated iron. (c) Why is the action referred to in (b) an important one?

9. Arrange the metals iron, sodium, calcium, potassium, and magnesium in the order of their decreasing chemical activity on water, or steam. Briefly present experimental evidence to justify your arrangement.

10. (a) List nine common metals that will liberate hydrogen from dilute sulphuric acid, or from hydrochloric acid. (b) Name five metals that will not liberate hydrogen from these acids. (c) Why is zinc commonly selected as the metal used in the laboratory preparation of hydrogen?

11. Describe the common laboratory method of preparing and collecting hydrogen. Include a labelled diagram of the apparatus used and a word equation for the chemical reaction involved.

12. In the preparation of hydrogen: (a) Why must dilute sulphuric acid be used instead of the concentrated acid? (b) What important precaution must be taken in preparing this dilute acid? Why? (c) Why is there a danger of a possible explosion in generating hydrogen? How is this avoided?

13. When common salt is placed in water it disappears, or diminishes in volume. When granulated zinc is placed in dilute sulphuric acid it also disappears, or diminishes in volume. Explain what happens in each case.

14. Recopy and complete the following word equations:

- (a) Magnesium + Sulphuric acid (dilute) $\longrightarrow$
- (b) Aluminum + Sulphuric acid (dilute) $\longrightarrow$
- (c) Iron + Sulphuric acid (dilute) $\longrightarrow$
- (d) Magnesium + Hydrochloric acid $\longrightarrow$
- (e) Aluminum + Hydrochloric acid $\longrightarrow$
- (f) Iron + Hydrochloric acid $\longrightarrow$

15. (a) Make a labelled drawing of a Kipp's apparatus suitable for generating hydrogen gas showing its appearance when the tap is open. (b) Draw the same Kipp generator when the tap is closed and the apparatus has been allowed to stand for some time. (c) Describe the Kipp generator drawn in (a) and (b) under the headings (i) construction features, (ii) how it operates. (d) What other gases are commonly held in reserve in Kipp generators, when cylinders of these gases are not readily available?

16. (a) What is water gas and why is it important? (b) Write a word equation for the preparation of this gas.

17. (a) List seven physical properties of hydrogen gas. (b) A student preparing hydrogen from zinc and dilute sulphuric acid smells the gas and observes a very disagreeable odour. The text description of physical properties states that hydrogen is an odourless gas. Account for this apparent disagreement.

18. Briefly describe experiments to show that hydrogen is (i) lighter than air, and (ii) not very soluble in water.

19. How could you prove that one of the chemical elements present in a

sheet of newspaper is hydrogen?

20. Describe an experiment which shows that water (hydrogen oxide) is formed when dry hydrogen is burned from a metallic jet. Include in your answer a labelled diagram of the apparatus used and a word equation for the burning process.

21. Describe a safe method for lighting the hydrogen gas escaping from a jet.

22. (a) What two chemical properties of hydrogen are shown by inserting a blazing splint up into an inverted bottle filled with this gas? (b) Why is it imperative that the bottle of hydrogen be held in an inverted position? (c) By what test can hydrogen be distinguished from all other gases?

23. (a) Make a labelled diagram of the apparatus used to show the reducing action of dry hydrogen on heated cupric oxide. Include a word equation for this reaction. (b) Why is it necessary to dry the hydrogen before passing it over the heated oxide? (c) Write a descriptive paragraph covering the experiment illustrated in (a) and include the following terms in your answer: reducing agent, oxidizing agent, reduction, oxidation, the product of reduction, the product of oxidation, the substance oxidized, and the substance reduced.

24. (a) Explain the statement: "For every oxidation there is an accompanying reduction." (b) List five elements which cannot be prepared from their oxides by reduction with hydrogen. (c) Write word equations for: (i) The passing of hydrogen over heated magnetic iron oxide. (ii) Heated cupric oxide is reduced with powdered coke.

25. Recopy and complete the following word equations:

(a) Hydrogen + Chlorine (in the presence of sunlight) $\longrightarrow$

(b) Hydrogen + Sulphur (molten) $\longrightarrow$

(c) Hydrogen + Nitrogen (under pressure + a catalyst) $\longrightarrow$

26. What are the chief commercial uses of hydrogen?

27. What are the advantages and disadvantages of using hydrogen and helium in balloons and dirigibles?

28. What is the source of the helium used by the United States for military purposes?

29. Describe an atomic hydrogen torch. Why is it commonly used in preference to an oxy-acetylene flame?

B

1. A certain sample of sulphuric acid contains 2.02% hydrogen by weight. How many grams of hydrogen could be prepared by the action of excess zinc on 98 gm. of this acid?

2. A current of dry hydrogen is passed over 14.31 gm. of heated cupric oxide. At the end of the experiment 11.43 gm. of metallic copper remain and 3.24 gm. of water are formed. Find the proportion of oxygen to hydrogen, by weight, in water.

3. In an experiment 53.821 gm. of cupric oxide were heated in contact with dry hydrogen. The metallic copper that was left weighed 42.989 gm. and 12.197 gm. of water were obtained. From this information calculate the percentage composition of water by weight.

CHAPTER 7

Water: The Universal Solvent

Water is absolutely indispensable to both animal and vegetable life; it is the cause of many of the most striking phenomena in nature; and it is employed for countless purposes by man.

P. F. FRANKLAND

For hundreds of years, water was thought to be an element, because it had never been broken down into simpler substances. Cavendish and Lavoisier, at the beginning of the nineteenth century, proved that water was a compound of the two colorless gases, oxygen and hydrogen.

Occurrence. Water is our most useful and abundant compound. Great bodies of water cover about five-sevenths of the earth's surface, extending in places to a depth of over five miles. In the polar regions and on high mountains, it occurs as vast quantities of ice and snow. Even some of the solid rocks of the earth's crust hold water in chemical combination. It is present in all fertile soil, and in the vapour state it is a variable but important component of the atmosphere, from which it condenses and is **precipitated** in various forms. All living tissues, both plant and animal, contain water, and hence it forms an important part of our common foods. Such foods as tomatoes, cucumbers, lettuce, and cabbage contain more than 90% water. Milk has about 87%, and lean beef and eggs almost 74%. Nearly 79% of our body weight is water, the amount varying from 90% in the blood to a very small percentage in the bones and teeth.

Importance. Water is the most important of all chemical compounds. In chemistry, its importance stems largely from its remarkable ability to dissolve other substances, including solids, gases, and other liquids. It is sometimes called "the universal solvent" because it will dissolve a portion of almost every known substance. The amounts dissolved are not necessarily large, but water's unique ability to dissolve substances accounts for its common use in making solutions. So many chemical reactions depend upon the presence of water that **inorganic** chemistry is largely the chemistry of water solutions.

Natural waters. Because of the great solvent action of water, all natural waters contain a variety of substances in solution. Rain water is relatively pure since it is formed by the condensation of water vapour and has been in contact only with the atmosphere. Atmospheric

oxygen, nitrogen, and carbon dioxide may be taken into solution as the drops fall through the air, and even solid dust particles may be included in the drops. As soon as the rain strikes the surface of the ground, it begins at once to dissolve soluble materials from the soil, rocks, and vegetation. Before it forms lakes and rivers, some of this water flows along the surface becoming more and more heavily laden with dissolved mineral salts. Much of it finally reaches the oceans, and ocean waters have a dissolved mineral-salt content of about 3.5%. Approximately 2.5% of sea water is common salt and the remaining salt content is chiefly composed of compounds of calcium, magnesium, iron, and potassium.

Rain water may penetrate deeply into the soil and underlying rocks and emerge later as a spring or well. Since the soil acts as a filter, this water may be clear and sparkling, but it will contain minerals dissolved from the soil. In limestone regions this soil water becomes very hard since it dissolves certain calcium and magnesium compounds. Hard waters are generally objectionable. They demand a wastage of soap before a lather can be produced, and leave a deposit of scale in steam boilers that results in clogging as well as fuel wastage. Many river waters contain not only substances in solution, but also suspended matter in the form of fine clay and sand that give the waters a turbid appearance. Organic matter from aquatic plant life, from fragments of vegetation, and from sewage may also be carried in suspension and may make the water unfit for drinking purposes. Any bacteria, feeding on this organic matter, multiply at a prodigious rate.

When water is clear, free from harmful germs, and minus objectionable dissolved chemicals, it is considered good drinking water and is called **potable** water. Water may have a bad odour and taste but still be safe to drink if the bacteria present are not disease-producing. Such water is said to be **polluted**. If, however, water contains harmful disease-producing germs, it is known as **infected** water and can only be made safe for drinking by boiling or by other treatments that will kill all such germs.

Purification. One of the most important problems facing every community is that of obtaining an adequate supply of good drinking water.



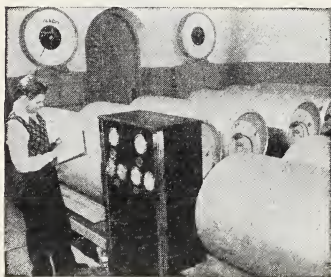
Permutit Company

Fig. 7.1. Scale formed in boiler tubes. Such deposits, caused by hard water, result in a great waste of fuel.

Most communities are compelled to purify their water supply by one or more of the following processes, and the process or combination of processes selected depends on the nature of the impurities in the water:

1. *Aeration*. Some cities aerate their water supply by spraying it into the air or by allowing it to run over an incline in thin sheets to bring it into contact with the oxygen of air and the ultra-violet rays of sunlight. The oxidation of objectionable organic matter improves the taste of the water and also kills many bacteria.

2. *Settling basins (sedimentation)*. Very muddy water, or water charged with sewage and other suspended matter, is often temporarily stored in large settling tanks. Here the coarser suspended matter gradually settles and the surface water can then be drawn off for further treatment.



C. I. L.

Fig. 7.2. Chlorine from the large tanks is fed into the water purification system of the Montreal Waterworks. Rate and volume of flow is controlled and measured by automatic instruments.

3. *Alum treatment (coagulation)*. A turbid, or coloured, water supply is often treated with small amounts of aluminum sulphate or with a mixture of alum and slaked lime. This treatment causes the formation of a white, jelly-like precipitate that slowly settles to the bottom and carries with it much of the suspended matter, at the same time removing the colouring matter and some bacteria.

4. *Sand filtration*. If the alum treatment is followed by filtration through extensive beds of sand and gravel floored with drainage tile, most of the suspended particles, including some bacteria, will be effectively removed. It should be noted, however, that filtration does not remove dissolved matter from the water.

5. *Chlorination or ozonation*. Even after filtration, water contains some bacteria. A common method of purification is treatment by small quantities of chlorine, either as liquid chlorine supplied from cylinders, or as bleaching powder (chloride of lime). Ozone, an allotropic form of oxygen (p. 172), is sometimes used instead of chlorine, especially in European cities. The explanation of the reaction is essentially the same for both chlorine and ozone; atomic oxygen, liberated by each substance, destroys the germs by oxidation.

Chlorine frequently acts on industrial wastes in the water to produce substances with objectionable tastes. However, when chlorine is

added in excessive quantities (super-chlorination), some of these objectionable tastes are removed. The objectionable chlorine taste that would then be present is removed with sulphur dioxide (Chapter 19).

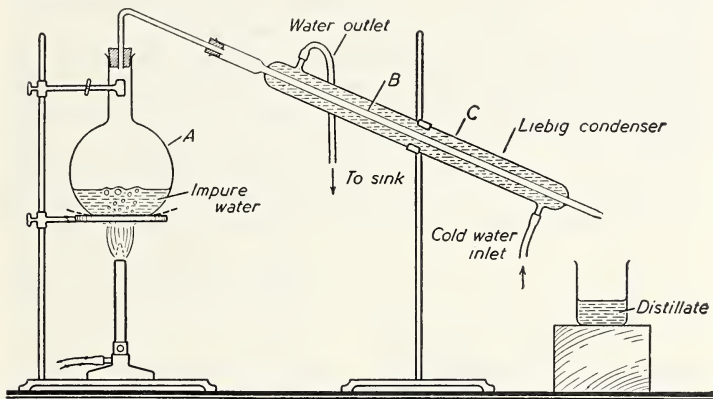


Fig. 7.3. The distillation of water using a Liebig condenser. The non-volatile substances remain in the flask and distilled water is collected as the distillate.

Distillation of water. The methods of purification just discussed are quite effective in producing wholesome drinking water suitable for most domestic uses. No one method is designed to produce pure water in the chemical sense, since most of the *dissolved* impurities are unaffected by these treatments. To prepare chemically pure water for scientific use, advantage is taken of the fact that water is easily changed into steam. Most of the dissolved substances are not volatile and remain in the vessel in which the water is boiled. Distillation is a double process involving two changes of state: **vaporization** of a liquid, and its subsequent **condensation**.

In Fig. 7.3, natural water is boiled in the flask (A), and the resulting steam is condensed while passing through the inner tube (B) of the Liebig condenser. A stream of cold water, flowing through the outer glass jacket (C), keeps the inner tube cold. As a result of this treatment, distilled water, freed from all dissolved and suspended matter, falls from the lower end of the tube. This **distillate**, when collected in a clean separate container, has a flat insipid taste. The first portion of the distillate may contain traces of redissolved gases and is usually discarded. **Ordinary distillation** is a process whereby a volatile solvent is separated from non-volatile solutes (Chapter 8).

Fractional distillation. Frequently it is desirable to separate a mixture of several liquids that have different boiling points. This can be accomplished by **fractional distillation**, a process necessitating controlled heating. The liquid with the lowest boiling point will distil off first, then the liquid with the next lowest boiling point, and so on. Each separate distillate is known as a **fraction**. Fig. 7.4 shows a distilling flask fitted with a thermometer, the bulb of which is just below the side-arm of the flask. Consider the changes that take place when the flask, containing a mixture of alcohol and water is heated. At normal pressure, ethyl alcohol boils at 78°C . whereas water boils

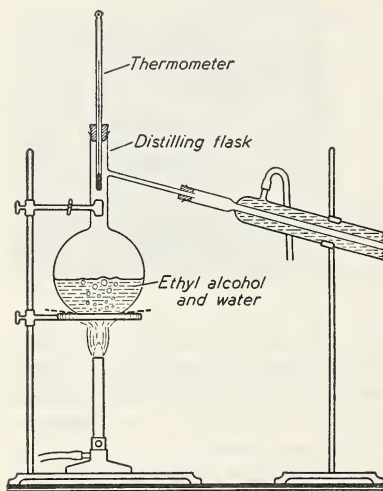


Fig. 7.4. Fractional distillation. Useful in separating liquids of different boiling points.

at 100°C . When the thermometer indicates a temperature of 78°C ., the mixture in the flask is agitated by the escaping alcohol vapour and a distillate, composed principally of alcohol but containing a little water, collects. The separation is not complete because water evaporates at temperatures below its boiling point, and considerable water vapour passes over with the alcohol vapour. The first fraction may be successively re-distilled to yield a purer product. Finally, a stage is reached where the distillate is 96% alcohol and 4% water and further distillation produces no further reduction in the water content.

Petroleum, or crude oil, is a mixture of a number of hydrocarbons (compounds containing only carbon and hydrogen) such as naphtha, gasoline, kerosene, lubricating oils, vaseline, paraffin, and other products. Because they have different boiling points, these fractions may be separated by heating the crude oil in large iron stills. This distillation will be explained in greater detail in Chapter 18.

Some complex solids such as coal and wood are decomposed when they are heated away from contact with air (dry distilled). The volatile products are condensed. This process is called **destructive distillation**, and will be discussed further in Chapter 17.

Physical properties of water. Water is a transparent liquid, colorless in thin layers but showing a distinct blue or bluish-green colour in large bodies. Pure water is odorless and tasteless, but good drinking water has a pleasant taste because it contains dissolved gases and minerals. Chemically pure water is an exceedingly poor conductor of electricity and heat.

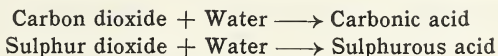
Some of the physical properties of water are used as standards of comparison when determining the corresponding physical properties of substances generally. Thus the weight of a substance, compared with the weight of an equal volume of water, is called its **specific gravity**. The gram, a unit of weight, is defined as the weight of 1 cc. of water at 4° C. In thermometry, the boiling point of water (at 760 mm.) is 100° C., and its freezing point (at 760 mm.) is 0° C. These two fixed temperatures can be determined easily by experiment. Water is also chosen as a standard for comparison in the measurement of the **specific heat** of various substances. Water has a **heat of vaporization** of 540 calories and a **heat of fusion** of 80 calories.

Chemical properties of water. 1. Water is such a stable compound (resists decomposition by heat) that even a temperature of 2000° C. causes a decomposition of less than 2%.

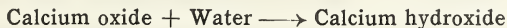
2. Water reacts with the more active metals, liberating hydrogen and forming a base:



3. Water reacts with oxides of non-metals (acid anhydrides) to form acids:



4. Water reacts with basic oxides to form compounds known as bases:



5. In many reactions, water acts as a catalytic agent, causing chemical changes that do not take place with perfectly dry materials. For example, phosphorus will not burn in perfectly dry air, but it will burn readily if even a trace of water vapour is present. Experiments have been performed to show that a mixture of perfectly dry hydrogen and oxygen will not explode when an electric spark is passed through the mixture.

6. Water causes acids, bases, and salts to dissociate into ions, a process that will be explained in Chapter 16.



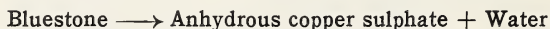
Baker Chemical Company

Fig. 7.5. Four hydrates commonly used in the laboratory.

Hydrates. Some substances, in crystallizing from a water solution, unite with a definite amount of water to form crystalline substances called **hydrates**. This water, unlike that trapped in crystals that decrepitate when heated, is a definite part of the substance formed. When hydrates are heated, they decompose to form **anhydrous salts** and water. This chemical reaction is called **dehydration**. Conversely, when water is added to an anhydrous salt, a hydrate is formed and heat is produced. This action is called **hydration**. If water is added to anhydrous copper sulphate, the salt turns from white to blue. This hydration is represented by the following equation:

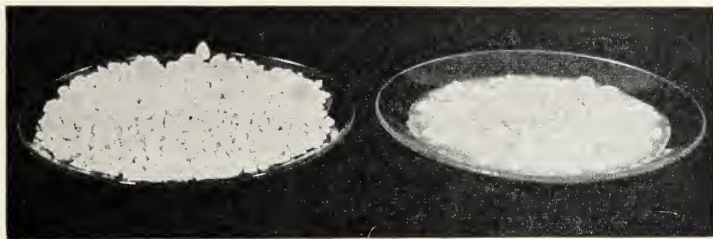


If a crystal of bluestone is heated in a test-tube, it quietly changes into a non-crystalline white powder, and drops of a colorless liquid appear on the sides of the tube. This liquid, when tested, proves to be water. This action is represented by the following word equation:



When the bluestone loses its water, it also loses its crystal form. The water contained in the hydrate is called **water of hydration** and is present in a fixed proportion by weight. Although this water of hydration is an essential part of the hydrate, it must not be assumed that all crystals are hydrates. Common salt crystallizes in perfect cubes but it is not a hydrate.

Certain hydrates hold their water of hydration so weakly that the crystals, when exposed to air, slowly lose their water of hydration,



Baker Chemical Company

Fig. 7.6. Deliquescence. *Right*, calcium chloride exposed to the air for several hours. *Left*, the same hydrate just removed from a stoppered bottle.

become covered with a white powder, and finally crumble into an anhydrous form. Such hydrates are said to be **efflorescent** and the action is called **efflorescence**. Washing soda and "hypo" crystals show this property in ordinary air, while bluestone will effloresce if the atmosphere is very dry.

Deliquescence. Another kind of action occurs when some very soluble solids are exposed to air. Calcium chloride absorbs moisture from the air to form a concentrated solution, and this property makes it useful to keep down road dust. This action is purely one of solution and is not a chemical change. Substances like calcium chloride, sodium hydroxide, and magnesium chloride, which may form solutions when exposed to air, are said to be **deliquescent**, and this action is called **deliquescence**. Such substances can be used as **drying agents** to remove moisture from various gases.

Test for water. A white powder, known as anhydrous copper sulphate, may be prepared by heating bluestone in a dry test-tube until its water of hydration is driven off. If this white powder changes to blue on the addition of a liquid, it may be assumed that the liquid is water or contains water.

More exacting tests have been devised that will detect the presence of water as well as determine its purity, but these are beyond the scope of the present treatment.

Composition of water. In studying chemical compounds, it is of great importance to be able to determine the exact quantity of the constituent elements of each compound. On page 100 there is a list of compounds that shows the percentage composition of each. This table shows that water has a fixed composition of 88.88% oxygen and 11.11% hydrogen, by weight. Again, on page 64 reference is made to the fact that water may be decomposed into the two gases, hydrogen and oxygen, in the ratio of 2 volumes of hydrogen to 1 volume of

oxygen. The composition of water can therefore be expressed either in volume units or in weight units. The methods used in determining the composition of water are typical of those used to determine the composition of other compounds.

Two general plans of attack are commonly used to determine the composition of any compound:

1. Decomposing the compound to find out what elements are present. This chemical process is called **analysis** (Gr. *ana*, a distribution; *lysis*, loosing).

2. Combining the elements to form the compound. This is known as **synthesis** (Gr. *syn*, with; *tithemi*, to place).

Analysis of water. The proportions (by volume) of hydrogen and oxygen, the elements composing water, may be determined by decomposing water by the passage of an electric current in the process called **electrolysis** (Fig. 7.7), making use of the **Hoffman apparatus**.

Since distilled water is a poor conductor of electricity, a small amount of sulphuric acid is added to make the water a better conductor. When the reaction ends, the amount of sulphuric acid is unchanged, but the amount of water has decreased.

The Hoffman apparatus operates as follows: With both stop-cocks open, the acidulated water is poured into the centre tube, which acts as a reservoir, until the two outer tubes are filled. The stop-cocks are then closed and the platinum electrodes are connected with a 6- to 10-volt storage battery or any other source of **direct current**. Platinum electrodes are used because this metal is very resistant to attack by most substances. As soon as the circuit is closed, small bubbles of a colorless gas collect on the surface of the electrodes and then rise through the acidulated water to gather at the top of the two outer tubes. As these gases collect, some of the water is displaced into the third vertical tube and forced into the reservoir at the top.

The gas collected over the negative electrode (cathode) is hydrogen. This can be shown by opening the stop-cock and collecting some of the gas in an inverted test-tube. When the tube is brought near a flame, the characteristic "pop" is heard and the gas burns with a pale-blue flame. Oxygen collects over the positive electrode (anode) and can be identified by opening the stop-cock and testing the escaping gas with a glowing splint as described in Chapter 4.

Regardless of the time the current flows, the volume of gas collected over the cathode is always twice the volume of gas collected over the anode. The whole experiment demonstrates that water is a compound consisting of two volumes of hydrogen combined with one volume of oxygen.

Synthesis of water. In contrast to analysis as accomplished by electrolysis, water can be built up from its constituent elements. To determine the composition of water (or any compound) by synthesis, two methods of computation may be used:

A. *Synthesis of water by volume.* The proportions by volume of hydrogen and oxygen that will unite to form water may be determined in a graduated tube called a **eudiometer**. This is a heavy-walled tube closed at one end. Near the closed end, two platinum wires are sealed through the glass with their ends almost meeting. This creates a spark gap across which an electric spark can be passed in order to ignite the mixture of gases in the tube. The resulting combustion takes the form of an explosion, producing water through the union of fixed proportions of the two gases.

The eudiometer is filled with mercury and inverted over the same liquid in a tall hydrometer jar, permitting adjustments in the mercury levels when the volumes of the enclosed gases are read. A small volume of hydrogen is next introduced and the eudiometer is then lowered so that the level of the mercury inside and outside the tube is the same. The enclosed hydrogen must therefore be under atmospheric pressure, and its volume is accurately read and recorded. About the same volume of oxygen is then introduced in the same manner, and after again adjusting the levels the total volume of the mixture is carefully read. An induction coil, operated by a 6-volt storage battery or several dry cells connected in series, is now connected with the platinum terminals of the eudiometer. The latter is

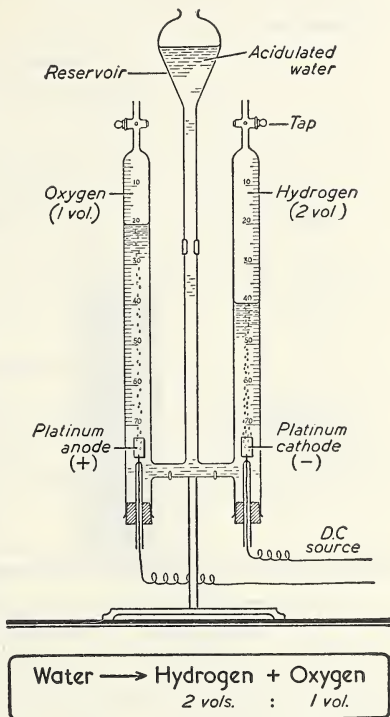


Fig. 7.7. The electrolysis of water using a Hoffman apparatus.

be under atmospheric pressure, and its volume is accurately read and recorded. About the same volume of oxygen is then introduced in the same manner, and after again adjusting the levels the total volume of the mixture is carefully read. An induction coil, operated by a 6-volt storage battery or several dry cells connected in series, is now connected with the platinum terminals of the eudiometer. The latter is

then grasped firmly and held down on a pad of rubber beneath the mercury while an electric spark from the coil is passed through the mixture. After the resulting explosion, the apparatus is allowed to cool so that the steam formed by the chemical union will condense to water of negligible volume. The levels of the mercury inside and outside the tube are again made to correspond, and an accurate reading of

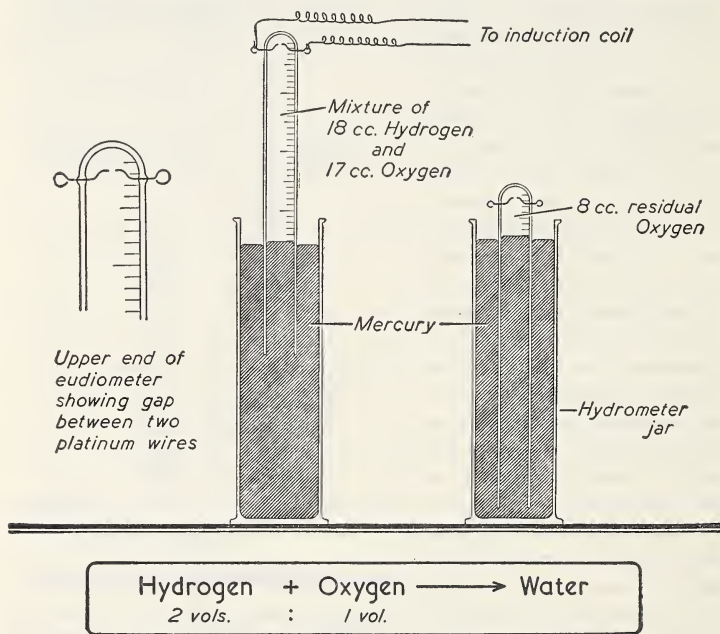


Fig. 7.8. Synthesis of water by volume in a eudiometer tube. *Left*, the mixture of gases before the explosion. *Right*, the residual gas after the reaction.

the volume of the unused (residual) gas in the eudiometer is then taken. If another spark is passed through the residual gas, nothing happens because only a portion of one of the two original gases remains after the explosion. (An excess of one gas should be planned at the beginning of the experiment, because the cushioning effect of the residual gas protects the eudiometer against the upward rush of the mercury after the explosion.)

Suppose that the measured volumes used in a particular experiment were as follows:

- | | |
|--|--------|
| 1. Volume of hydrogen introduced | 18 cc. |
| 2. Total volume of the mixture (hydrogen and oxygen) | 35 cc. |
| 3. Total volume of oxygen (by subtraction) | 17 cc. |
| 4. Volume of residual gas (proved to be oxygen by a glowing splint test) | 8 cc. |

It appears that 9 cc. of oxygen combined with all the hydrogen (18 cc.) to form water. Similarly had 22 cc. of hydrogen and 8 cc. of oxygen been introduced into the eudiometer and a spark passed, 6 cc. of hydrogen would have remained as a residual gas in the tube. It is only when two volumes of hydrogen are mixed with one of oxygen that the two gases totally disappear, but as previously mentioned this is an undesirable procedure. Regardless of the number of times the experiment is repeated, the result is always the same: 2 volumes of hydrogen combine with 1 volume of oxygen to form water.

B. *Synthesis of water by weight.* The composition of water by weight may be determined by the reduction of an oxide (such as cupric oxide) with dry hydrogen.

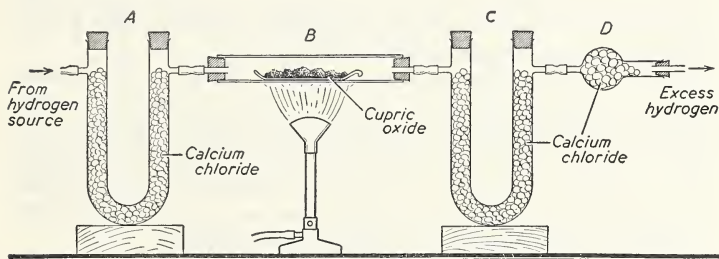


Fig. 7.9. The percentage composition of water by weight. This synthetic method was used by the great French scientist Jean Dumas and is often referred to as Dumas' method.

Hydrogen from a Kipp or cylinder enters on the left and is dried by passing it through a U-tube (A) containing a drying agent such as calcium chloride. The tube (B) contains cupric oxide and the weight of the ignition tube with its contents is recorded before the reduction begins. The dry hydrogen reduces the heated oxide forming copper and water (as a vapour). This vapour is carried along by the excess of hydrogen and absorbed in the calcium chloride tubes (C + D). The weight of (C + D) is also determined prior to the experiment. After the cupric oxide has been reduced, the apparatus is allowed to cool to room temperature. Then the tubes (B) and (C + D) and their con-

tents are re-weighed. The increase in weight of the tubes ($C + D$) represents the weight of the water formed. The loss in weight in (B) gives the weight of the oxygen used. The difference between the weight of the water formed and the weight of the oxygen used gives the weight of the hydrogen used. The following data are the results of such an experiment:

- | | |
|---|------------|
| 1. Wt. of tube (B) and cupric oxide before reduction | 42.901 gm. |
| 2. Wt. of tube (B) and contents after reduction | 41.701 gm. |
| (a) wt. of oxygen used (1)–(2) | 1.20 gm. |
| 3. Wt. of calcium chloride tubes ($C + D$) and contents after experiment | 50.87 gm. |
| 4. Wt. of calcium chloride tubes ($C + D$) and contents before experiment | 49.52 gm. |
| (b) wt. of water formed (3)–(4) | 1.35 gm. |
| (c) therefore weight of hydrogen used to create water (b)–(a) | 0.15 gm. |

Thus, in this particular experiment, 0.15 gm. of hydrogen have combined with 1.20 gm. of oxygen to form 1.35 gm. of water, or in round numbers, 1 part by weight of hydrogen combined with 8 parts by weight of oxygen in the synthesis of water.

The method just described was first used in 1819 by two scientists, Berzelius and Dulong. In 1842, the great French chemist, Jean Dumas, repeated more accurately the work of these earlier scientists. As a result of nineteen separate experiments, Dumas found that 840.161 grams of oxygen were used in the formation of 945.439 grams of water. The weights of hydrogen and oxygen thus ascertained stand in the ratio of 1 gram of hydrogen to 7.98 grams of oxygen.

In 1895, an American chemist, Edward Morley, synthesized water from pure hydrogen and pure oxygen. He more accurately determined the proportion to be 8 parts by weight of oxygen to 1.008 parts by weight of hydrogen.

The investigation of the nature of water produced new methods and techniques which became available to chemists for further research. The methods by which our knowledge of water has been expanded produced a pattern whereby many other more complex substances have been analyzed and synthesized.

EXERCISE

A

- (a) Write an account of the occurrence of water in nature. (b) Why is water regarded as the most important chemical compound?
- (a) How do surface waters collect impurities? (b) Compare rain water, soil water, and ocean water, with chemically pure water, and account for the

impurities present in each of the natural waters. (c) Why is rain water the purest of the natural waters?

3. (a) Distinguish between potable water and polluted water. (b) When is water said to be infected? How can infected water be made safe for drinking?

4. (a) What are the two methods used in the aeration of water? Why is each method effective? (b) What three properties of drinking water are improved by aeration?

5. In many cities the raw water undergoes in succession all the processes of sedimentation, coagulation, and sand filtration. Explain the effect of each process and explain why the order of treatment is important.

6. (a) What is the purpose of chlorinating water? (b) Why is super-chlorination more effective than ordinary chlorination? (c) What is one objection to super-chlorination and how is this objection overcome?

7. (a) Describe in detail how you would prepare chemically pure water from any of the natural waters. Make a labelled diagram of the apparatus. (b) What is the name of the process involved? Define this term. (c) Could chemically pure water be prepared from natural waters by repeated filtrations? Explain.

8. (a) What is meant by fractional distillation? (b) Describe how a sample of nearly pure methyl alcohol can be obtained from a solution of 50% alcohol and water.

9. (a) List five physical properties of water. (b) Explain the relation of water to (i) specific gravity, (ii) specific heat.

10. (a) List six chemical properties of water. (b) Explain each of the following statements: (i) Water is a stable compound. (ii) Water often acts as a catalytic agent.

11. (a) Define a hydrate. In your definition make clear the meaning of water of hydration. (b) Do crystalline solids always combine with water when they crystallize from a water solution?

12. Distinguish between hydration and dehydration and give one example of each.

13. Describe the visible changes observed when a crystal of bluestone is heated. Write a word equation for the reaction.

14. (a) Explain the terms efflorescence and deliquescence. (b) Name a salt that effloresces in ordinary air and describe an experiment to illustrate its efflorescence. (c) Name a salt that deliquesces in ordinary air and describe an experiment to illustrate its deliquescence.

15. Describe a test to determine the presence or absence of water in any liquid solution.

16. (a) Water collects on the outer surface of a tumbler filled with ice cubes. It also collects on the inner surface of a cold glass dish inverted over a burning candle. Explain the source of water in each case. (b) If you doubted that the colourless liquid seen, in either case, was water, how would you proceed to identify it?

17. Distinguish between an analysis and a synthesis.

18. (a) Describe an experiment to show the electrolysis of water. Make a labelled diagram of the apparatus used and include a word equation for the reaction. (b) In the electrolysis of water, why, (i) is direct current used, (ii) is a small quantity of sulphuric acid added, (iii) are platinum electrodes used? (c) What important property of water is shown by electrolysis? (d) Why is the

electrolysis of water an analysis by volume?

19. (a) Describe the structure of a eudiometer tube. (b) Describe an experiment in which a eudiometer is used to synthesize water, and make a labelled diagram of the apparatus used. (c) In the synthesis of water in a eudiometer, why would it be inadvisable to explode a mixture of 10 cc. of oxygen and 20 cc. of hydrogen?

20. (a) Make a labelled diagram of the apparatus used in the synthesis of water when its composition by weight is to be determined. (b) Describe in detail an experiment utilizing the apparatus drawn in (a). Indicate each weighing made and give a reason for each step in the procedure. (c) In the synthesis of water by weight, why is the hydrogen dried?

21. The history of the chemistry of water shows many interesting developments. What effect did the investigations into the nature of water have on the study of other compounds?

B

1. Calculate the ratio by weight of hydrogen to oxygen in water from the following data obtained by the reduction of heated cupric oxide by dry hydrogen:

Weight of cupric oxide + tube before experiment	65.90 gm.
Weight of tube and contents after the experiment	62.61 gm.
Weight of calcium chloride tubes before experiment	77.45 gm.
Weight of calcium chloride tubes after experiment	81.15 gm.

2. In an experiment to synthesize water, a chemist obtained the following results:

Weight of combustion tube + cupric oxide before experiment	88.25 gm.
Weight of combustion tube + contents after experiment	80.25 gm.
Weight of calcium chloride tubes at beginning of experiment	138.50 gm.
Weight of calcium chloride tubes at end of experiment	147.50 gm.

Find: (a) the weight of oxygen present in the water formed, (b) the weight of the water formed, (c) the weight of the hydrogen in the water formed, (d) the proportion by weight in which hydrogen and oxygen are present in water.

3. In an experiment, 53.821 gm. of copper oxide were heated in contact with dry hydrogen. The metallic copper that remained weighed 42.989 gm. and 12.197 gm. of water were obtained. Calculate from these data the percentage composition of water.

4. Calculate the ratio of hydrogen to oxygen by volume in water from the following data obtained by the eudiometer method:

Volume of oxygen introduced into eudiometer	16.8 cc.
Total volume of oxygen and hydrogen in eudiometer	42.0 cc.
Volume of gas left after explosion (oxygen)	4.2 cc.

5. If 50 ml. of hydrogen and 37 ml. of oxygen are exploded in a eudiometer over mercury, identify (neglecting water vapour) the remaining gas and give its volume. (All measurements made at the same temperature and pressure.)

6. In a eudiometer over mercury, 15 cc. of oxygen were collected. Hydrogen was passed into the eudiometer until the volume of the mixed gases was 22.4 cc. A spark was then passed through the mixture. What gas was left in the eudiometer? How would you identify it experimentally? What would be the volume of the remaining gas?

7. In a eudiometer tube, 30 cc. of hydrogen were mixed with 100 cc. of air containing 21% by volume of oxygen, and the mixture exploded. What was the composition and volume of the residual gas?

CHAPTER 8

Solutions

In the strictly scientific sense of the word, insolubility does not exist, and even those substances characterized by the most obstinate resistance to the solvent action of water may properly be designated merely as extraordinarily difficult of solution, not as insoluble.

O. N. WITT

Solution terms. Little did the alchemists, in their search for the universal solvent, suspect they had the nearest thing to it always at hand. One of the most important properties of water is its ability to **dissolve** so many different substances. There is scarcely a substance that does not dissolve in water to some extent. Even sand, glass, and gold are all slightly soluble, but because so little of them dissolves they are considered **insoluble**. When a pinch of salt is stirred in a beaker of water, the salt dissolves and forms a **solution**. The salt, or the substance dissolved, is called the **solute**, and the water that does the dissolving is the **solvent**. The resulting mixture is a **dilute solution**. If additional salt is used, the clear solution might be described as **more concentrated**. A small crystal of copper sulphate, stirred in a beaker of water, imparts a uniform blue colour to the whole solution, which nevertheless remains entirely transparent. Both the solute and the solvent will pass through a filter paper. All samples of a well stirred sugar solution seem to taste equally sweet. These facts indicate a uniform distribution of the solute throughout the solvent. So small are the particles of solute that they cannot be seen even with a powerful microscope. This uniformity and clearness of solutions is accounted for by the molecular dispersion of the solute (see p. 113). A solution has the same composition throughout, and is said to be a **homogeneous mixture**.

Types of solutions. The most common type of solution is a solid dissolved in a liquid. However, a solution may consist of any of the nine possible variations of a solid, liquid, or gas dissolved in a solid,

liquid, or gas. As some of these are unusual, only the most common types will be dealt with, namely:

1. Solids dissolved in liquids.
2. Gases dissolved in liquids.
3. Liquids dissolved in liquids.
4. Gases dissolved in gases.
5. Liquids dissolved in gases.

Solids in liquids. When clay is stirred in water, a **suspension** results. The clay has not dissolved and the mixture is *turbid*. If the mixture is allowed to stand, the coarser particles will settle out; if filtered, the clay will remain as a **residue** on the filter paper and the water, as a **filtrate**, will pass through.

Whether a solid will dissolve or not depends on the nature of the solid and of the solvent. Sand, iodine, and steel are practically insoluble in water while sugar is quite soluble. Although water is the commonest solvent, it is not the only one. Some substances, insoluble in water, will dissolve in other solvents. Iodine dissolves readily in alcohol forming a brown solution sold under the name of **tincture** of iodine. Because carbon tetrachloride is an excellent solvent for grease, it is used in the dry cleaning industry.

The proportion of solute to solvent in a solution is sometimes represented by *per cent*. Thus a "3% solution of iodine" means that the solution contains 3 parts by weight of iodine to 97 parts by weight of the solvent; i.e. 3 parts by weight of solute in 100 parts by weight of solution.

Rate of solution of solids in liquids. A lump of sugar will dissolve more rapidly in hot than in cold water, and if the lump is first pulverized it will dissolve still more rapidly. Stirring will further hasten the rate of solution. Thus the factors influencing the speed of the dissolving process are three in number:

1. *Temperature*. Most solids dissolve more rapidly if the solvent is warmed.

2. *Area of surface*. The greater the surface area of the solute, the faster it will dissolve.

3. *Agitation*, or stirring, speeds the dissolving process. Previously, reference was made to the solution formed by stirring salt with water. Even without stirring, the salt in time would have **diffused** completely through the water to form eventually a homogeneous mixture.

A small crystal of bluestone placed at the bottom of a tall cylinder of water diminishes in volume as it diffuses through the solvent. The kinetic energy of the molecules (p. 113) causes them to leave the surface of the solid, thus exposing new surfaces of the solute. This

continues together with the subsequent intermingling with water molecules. It may take several months for the solution to have the same "blueness" throughout, but eventually the mixture becomes truly homogeneous.

Gases in water. A beaker of cold "tap water" contains dissolved air and is perfectly clear. If the beaker is allowed to stand in a warm room, the temperature of the solution rises and bubbles of oxygen and nitrogen come out of the solution. The fact that atmospheric oxygen dissolves in water is of great importance in nature because this dissolved oxygen enables aquatic plants and animals to breathe. Dissolved oxygen is also important because it aids decay through oxidation of dead organisms that would otherwise accumulate and pollute all waters. Some gases, like ammonia, are very soluble in water; others, like hydrogen, are only slightly soluble. All gases are more soluble in cold water than in hot, and their solubility is also increased by an increase in pressure. In the manufacture of soft drinks, carbon dioxide under pressure is dissolved in a flavoured sugar solution, and the bottle is capped to prevent the escape of gas. When the cap is removed the decreased pressure permits some of the gas to escape and the familiar **effervescence** results.

Liquids in water. Some liquids (alcohol, sulphuric acid, and vinegar) will mix with water in all proportions to form solutions. They are said to be **miscible**. Other liquids (gasoline, mercury, and carbon disulphide) are almost completely insoluble in water and will not form solutions with it. They are said to be **immiscible**. If kerosene is shaken with water, the mixture soon separates into two layers. If soap is added and the mixture again shaken, the soap surrounds the tiny droplets of kerosene and keeps them apart. The droplets will remain dispersed in the water for a long time. Such a suspension of one liquid in another is called an **emulsion**. Soap is an emulsifying agent. An emulsion is not a solution but a **mechanical mixture** of one liquid in another liquid in which separation takes place very slowly. Mayonnaise dressing is an emulsion of oil and vinegar, with egg added as the emulsifying agent. In common with other emulsions, milk is not clear like a solution but is turbid. Some liquids, **partially miscible**, lie between alcohol and carbon disulphide in the manner in which they mix with water. Ether will dissolve in water to a certain extent, and then it becomes immiscible in the solution. Two layers will form, the top one consisting of the solvent ether with dissolved water, and the bottom layer composed of a solution of ether in water.

Gases in gases. All gases are miscible with one another in all proportions regardless of their densities. Hence no separation of the

atmospheric gases takes place. Air is a homogeneous mixture and is therefore a true solution.

Liquids in gases. Water, exposed to air, evaporates. Just as salt dissolves in water to form a solution, so does water, when evaporated, dissolve in air. **Relative humidity** is the term used to express the relationship between the mass of water vapour dissolved in a certain volume of air and the mass of water vapour the same air could hold if saturated at the same temperature. Thus, when the relative humidity is 40%, the air is holding in solution 40% of the water vapour it could hold at the same temperature if it were saturated. The temperature at which the air is saturated with water vapour is known as the **dew-point**.

Saturated and unsaturated solutions. When a small amount of sugar is added to some water in a flask and shaken, the sugar soon dissolves to form a solution. If a little more sugar is added and the process repeated, this sugar also dissolves but this time the dissolving occurs more slowly than previously. Eventually, however, a condition will be reached when additional quantities of sugar will not dissolve. Even after shaking, some of the sugar settles to the bottom of the flask. No amount of agitation will cause this excess sugar to dissolve in the solution. The clear solution above the excess sugar is said to be **saturated**. A saturated solution contains as much of the solute as it can possibly dissolve when in contact with an excess of the solute at a particular temperature. The other solutions in which more sugar could be dissolved by merely shaking were **unsaturated** solutions at that particular temperature.

If the saturated solution of the sugar in water plus the excess sugar is heated, the heating increases the water's capacity to dissolve sugar, and the excess sugar may disappear, and a hot, possibly unsaturated, solution will result. If sufficient sugar is added to this clear hot solution and the mixture shaken again, a saturated solution with some excess solute is obtained. For every temperature there is a definite quantity of solute that will dissolve in a definite quantity of solvent to form a saturated solution. Most solids are more soluble in hot water than in cold. If a hot saturated solution is cooled, some of the solute ordinarily comes out of solution in characteristic geometric shapes called **crystals**. Common salt and sugar crystals are cubical in shape, ordinary saltpetre forms needle-like crystals, and alum crystals are eight-sided. Just enough of the solute crystallizes out during the cooling to keep the solution saturated at the lower temperature.

Supersaturated solutions. It is possible, however, to prepare a solution containing more dissolved solute than would be contained in

a saturated solution at the same temperature. If hot saturated solutions of a few substances such as sodium sulphate, sodium acetate, and sodium thiosulphate ("hypo") are carefully cooled, the excess solid may not crystallize out. The resulting cold solution holds a great deal more solute than a saturated one would at that same temperature. Such a solution is called a **supersaturated solution**.

If, however, a crystal of the solute is dropped into the supersaturated solution, a rapid crystallization begins and will continue until enough solute precipitates out of solution to leave the solution saturated. When crystallization occurs, the solution becomes quite warm, as heat is generated by the solid coming out of solution. As with unsaturated solutions, an indefinite series of supersaturated solutions can be prepared. Some may have only a few grams more solute than a saturated solution, and others may have a great deal more solute dissolved in the same quantity of solvent. Thus, for a given temperature, the saturated solution is the only one having a definite amount of solute dissolved in a given amount of solvent.

Solubility. *The term solubility is defined as the weight of the solute, usually expressed in grams, that will dissolve in a given amount of the solvent (usually 100 grams of water) to form a saturated solution at a given temperature.* Thus the statement that the solubility of potassium nitrate at 15°C . is 21 grams means that 21 grams of potassium nitrate will dissolve in 100 grams of water to form a saturated solution at 15°C . The solubility of potassium nitrate at 50°C . is 85 grams. The solubility of potassium nitrate increases enormously as the temperature rises, but that of common salt changes very slightly. If the solubility of a salt is determined experimentally at various temperatures, a graph known as a **solubility curve** may be drawn. Such graphs are very useful in showing the variation in solubilities at different temperatures (Fig. 8.1).

Factors affecting the solubility of solids in liquids. A study of the solubility curves shows that in most cases the solubility of a salt increases as the temperature increases, and that the degree of solubility depends on the nature of the solute. The solubility also depends a great deal on the nature of the solvent, but pressure has little or no effect on the solubility of solids in liquids.

The formation of crystals. The amount of solute that can be held in solution is decreased either by a drop in temperature or by evaporation of the solvent. When either occurs, the excess solid comes out of solution in the form of crystals. If a string is hung in a hot concentrated solution of alum in an open beaker and left for several days, large crystals will form on the string. These crystals always have a definite

structure. If evaporation takes place slowly, the crystals formed are usually large and complete. If the evaporation is rapid, the crystals are smaller and incomplete.

When crystals are formed by any of the above methods, they often entrap small quantities of water. When a crystal thus formed is heated, the entrapped water boils, and the resulting steam explodes the crystal producing a crackling sound like that noted when potassium chlorate crystals were heated. This is called **decrepitation**.

EXERCISE

A

1. Define, giving examples in each case: solute, solvent, solution, dilute solution, concentrated solution.

2. Name five solvents other than water which are commonly used, and give at least one solute that will dissolve in each.

3. A solution of common salt (sodium chloride) containing 35 grams of solute dissolved in 100 grams of water at 40° C. is said to be concentrated, while a solution of potassium nitrate containing 35 grams of solute dissolved in 100 grams of water at 40° C. is said to be dilute. Explain.

4. What is the meaning of the term homogeneous?

5. List five common types of solutions, illustrating your answer by an example in each case.

6. Discuss three factors that affect the rate of solution of a solid in a liquid.

7. Describe an experiment illustrating the diffusion of copper sulphate in a water solution and explain this phenomenon.

8. (a) Compare the effect of (i) temperature, and (ii) pressure, on the solubility of a gas in water. (b) Account for the effervescence seen when ginger ale has been poured into a tumbler. (c) State the importance of the dissolved oxygen present in the natural waters of lakes and streams.

9. List three factors that affect the solubility of solids in liquids, and illustrate each with an example.

10. (a) What are miscible liquids? Give three examples. (b) Name three pairs of immiscible liquids. (c) Distinguish between a suspension and an emulsion, giving an example of each.

11. (a) Define each of the following: an unsaturated solution; a saturated solution; a supersaturated solution. (b) Give two common methods for expressing the concentration of a solution.

12. How could you distinguish experimentally between an unsaturated, a saturated, and a supersaturated solution of the same solute?

13. (a) What is meant by the solubility of a salt? (b) Explain how you could experimentally determine the solubility of a particular solid in water at 35° C.

14. (a) How could you prepare large, well-shaped crystals of alum or copper sulphate? (b) Sugar crystals are often found in jars of honey and maple syrup although neither evaporation nor cooling has taken place. Explain. (c) What is the explanation of the phenomenon known as decrepitation?

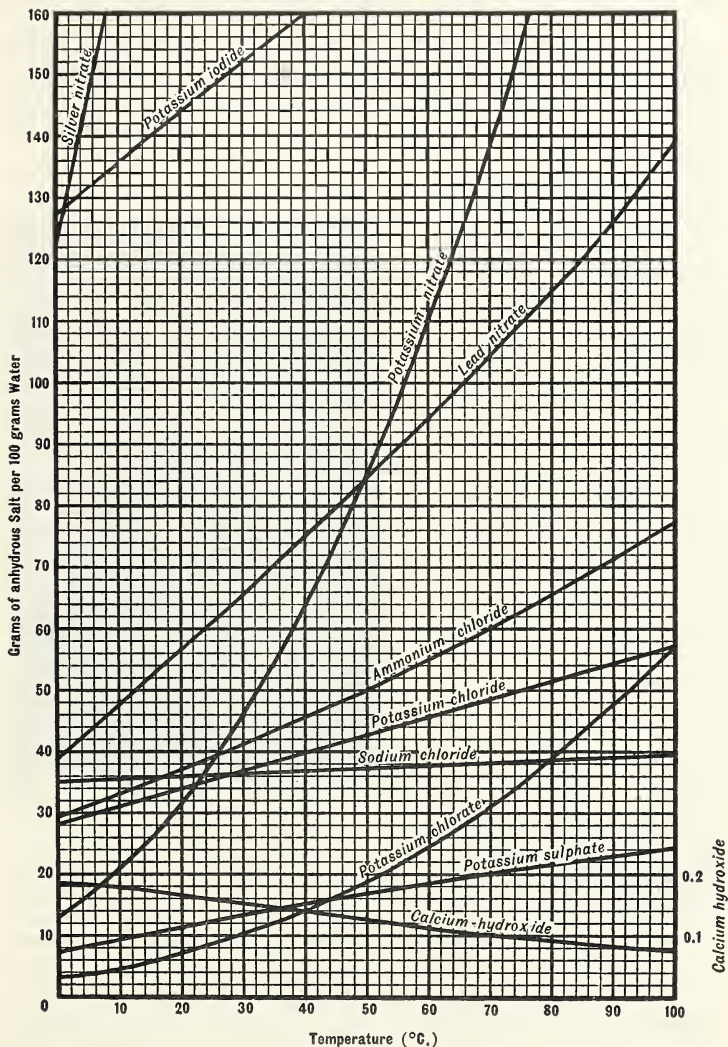


Fig. 8.1. Solubility curves for ten substances in water. Note that the solubility curve for calcium hydroxide is shown with different ordinates than the curves for the other substances.

B

When chemists, by experiments, have ascertained the solubilities of various solids in water at various temperatures, this information can be recorded in tables, or may be shown graphically by solubility curves similar to those shown in Figure 8.1. The latter method is more convenient and informative than tables, since these curves give the solubilities at all temperatures instead of at a few stated points.

In these graphical expressions of solubility, the abscissae of the squared paper represent temperatures, while the ordinates represent the solubilities of the anhydrous salts per 100 grams of water, i.e., starting from the left-hand corner of the graph, increases in temperature are represented in a horizontal direction and increases in concentration in a vertical direction.

Inspection of Figure 8.1 shows that a wide diversity exists in the slope of the solubility curves shown. Most of them slope upward, indicating that most solids behave like sugar in being more soluble in hot water than in cold. A few, however, such as slaked lime, decrease in solubility as the temperature rises. The solubility of sodium chloride (common salt) is only slightly affected as the temperature is increased.

Let us create a solubility curve from the following data obtained in experiments on the solubility of potassium nitrate (ordinary saltpetre):

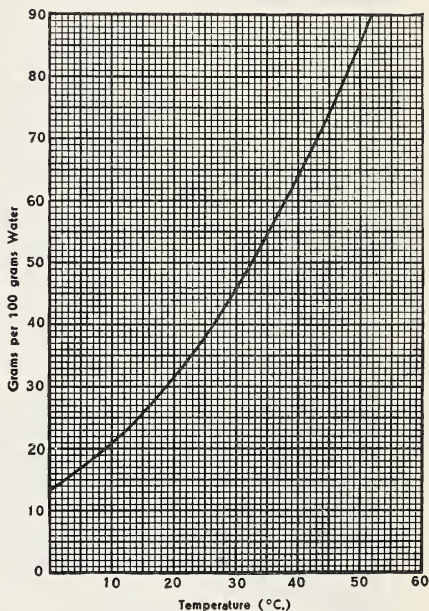


Fig. 8.2. A solubility curve for potassium nitrate in water.

Temperature in C°.	0°	10°	20°	30°	40°	50°
Solubility per 100 gm. water	13 gm.	21 gm.	32 gm.	46 gm.	64 gm.	85 gm.

(a) What is the solubility of potassium nitrate at 35° C.? At 45° C.? (b) At what temperature will 100 gm. water dissolve 50 gm. potassium nitrate to form a

saturated solution? What weight of solute would be deposited if this solution were cooled to $12^{\circ}\text{C}.$? (c) At what temperature will a saturated solution of potassium nitrate contain exactly 20% by weight of the solute?

1. Calculate the solubility of potassium chlorate in water at $40^{\circ}\text{C}.$ If 25.6 grams of water at this temperature dissolve 3.71 gm. of this salt in forming a saturated solution. Give your answer as grams of potassium chlorate per 100 gm. of water.

2. In an experiment to determine the solubility of a particular salt, an empty evaporating dish was found to weigh 28.6 gm. When partly filled with a saturated water solution of the salt at $50^{\circ}\text{C}.$, the dish weighed 52.2 gm. After the solution had been carefully evaporated to dryness, the dish and its contents weighed 34.68 gm. Calculate the solubility of this salt in water at $50^{\circ}\text{C}.$

3. Calculate the solubility of potassium nitrate at $65^{\circ}\text{C}.$ from the following weighings:

Weight of empty evaporating dish 63.45 gm.
 Weight of dish + saturated solution of this salt at $65^{\circ}\text{C}.$ 212.07 gm.
 Weight of dish + solid potassium nitrate 145.72 gm.

4. Using squared paper, draw the solubility curve for silver nitrate in water from the following data:

Temp.	Solubility (gm./100 gm. water)	Temp.	Solubility (gm./100 gm. water)
$0^{\circ}\text{C}.$	115 gm.	$60^{\circ}\text{C}.$	470 gm.
$10^{\circ}\text{C}.$	160 gm.	$70^{\circ}\text{C}.$	550 gm.
$20^{\circ}\text{C}.$	215 gm.	$80^{\circ}\text{C}.$	650 gm.
$30^{\circ}\text{C}.$	270 gm.	$90^{\circ}\text{C}.$	760 gm.
$40^{\circ}\text{C}.$	335 gm.	$100^{\circ}\text{C}.$	910 gm.
$50^{\circ}\text{C}.$	400 gm.		

From a study of this solubility curve answer the following questions: (a) What will be the concentration of a saturated solution at $32^{\circ}\text{C}.$? At $76^{\circ}\text{C}.$? At $5^{\circ}\text{C}.$? (b) At what temperature will the concentration of a saturated solution be (i) 600 gm./100 gm. water? (ii) 350 gm./100 gm. water? (iii) 725 gm./100 gm. water? (c) If you were given a particular solution of silver nitrate at $55^{\circ}\text{C}.$ containing 175 gm. of solute per 100 grams of water: (i) Is this solution unsaturated, saturated, or supersaturated? (ii) If this solution were cooled, at what temperature would it become saturated? (d) If you were given another silver nitrate solution at $30^{\circ}\text{C}.$ containing 215 gm. of silver nitrate per 100 grams of water: (i) What kind of solution is it? (ii) If the solution were cooled, at what temperature would it become saturated?

5. From a study of the solubility curves shown in Figure 8.1 answer the following questions: (a) Find the solubilities of the following compounds at the temperatures indicated: (i) Potassium chlorate at $15^{\circ}\text{C}.$, at $45^{\circ}\text{C}.$, at $75^{\circ}\text{C}.$? (ii) Lead nitrate at $5^{\circ}\text{C}.$, at $25^{\circ}\text{C}.$, at $35^{\circ}\text{C}.$? (b) At what temperature will 100 grams of water dissolve equal weights of potassium chlorate and potassium chloride? (c) At what temperature are the solubilities of sodium chloride and

potassium nitrate identical? (*d*) A certain solution of potassium chloride at 50°C . contains 14 grams of solute per 100 grams of water. How many grams of the salt must be added to saturate it? (*e*) By how many grams of solute does the solubility of lead nitrate exceed that of potassium sulphate at 60°C .? (*f*) What weight of ammonium chloride is necessary to saturate 65 grams of water at 50°C .?

CHAPTER 9

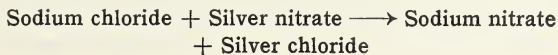
Chemical Classification

It is sufficiently clear that all things are changed, and nothing really perishes, and that the sum of matter remains absolutely the same.

FRANCIS BACON

The Law of Conservation of Mass. Lavoisier discovered that mercury, heated in air, increased in weight, and that the increase in weight was exactly equal to the weight of that part of the air used up in the formation of a new substance (Chapter 3). Magnesium, lead, copper, and other substances also gain in weight when heated in air, and the gain in weight is equal to the weight of oxygen used in the chemical action. Before the study of classification is begun, it is necessary to explore the significance of the investigations concerning increases in weight. It should be noted that (1) new substances are formed in each of the above instances, and (2) there has been no change in total weight during any of these reactions. The question arises, "Is this typical of every chemical reaction?" To answer the question adequately would necessitate studying every chemical reaction. Since such an undertaking is impossible, only a few reactions will be discussed here.

A silver nitrate solution is poured into a test-tube and the test-tube placed carefully upright in a flask containing a solution of common salt so that the two clear solutions cannot mix, and a stopper is inserted firmly in the flask as shown in Fig. 9.1A. The stoppered flask containing the two separate solutions is carefully weighed. Then the flask is inverted to allow the solutions to mix as shown in Fig. 9.1B. A thick, curdy white **precipitate** is immediately formed. *A precipitate is an insoluble solid formed as a new substance when a chemical reaction takes place between solutions.* It is evident that in this experiment a chemical change has taken place, because a new substance, differing in properties from the two original substances, has been formed. When the stoppered flask is now reweighed it is found that there has been no change in weight. The following word equation represents this reaction:



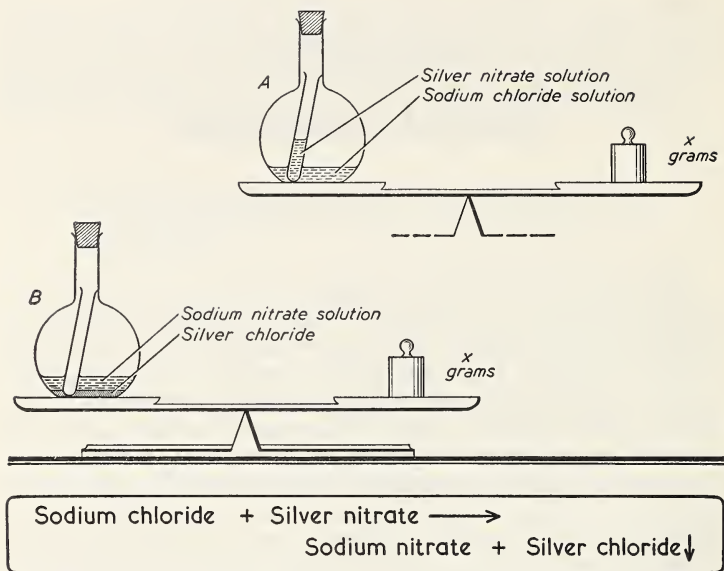
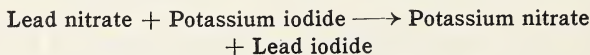


Fig. 9.1. The Law of Conservation of Mass. When the solutions in *A* are mixed, a chemical change takes place. The products of the reaction in *B* weigh the same as the original solutions.

The insoluble precipitate formed is silver chloride. This experiment can be repeated using different pairs of solutions. If lead nitrate and potassium iodide solutions are used, a bright yellow precipitate of lead iodide is formed, and again there is no loss or gain in weight.



It may be argued that when a candle burns, there appears to be a decided loss in weight as nothing seems left behind after the oxidation. In this case, the products of the reaction are invisible gases that are difficult to catch and weigh. However, this has been done, and it has been found that the weight of the candle used, plus the weight of the oxygen used, is exactly equal to the weight of the products of the combustion. Many hundreds of chemical reactions have been investigated and in every instance it has been found that *the total weight of the substances formed in any chemical reaction is exactly equal to the total*

weight of the substances that have undergone the change. A generalized statement telling how matter behaves under certain conditions is called a **Law**. The law just developed is called the **Law of Conservation of Mass** or the Law of Conservation of Matter. It is sometimes stated as "Matter is neither created nor destroyed in any chemical change." The quantity of matter in a body is called its **mass**, while its **weight** is a measure of the **force** of attraction of the earth upon it. The weight of a body depends upon (1) its mass, and (2) the distance of the body from the earth's centre. Hence weight will change with altitude while mass remains the same. Therefore, it is more accurate to refer to the law as the Law of Conservation of Mass rather than "of Weight". However, the mass of a body is in practice (as above) usually measured by its weight since the factor of distance is a constant in the laboratory.

Law of Definite Proportions. In Chapter 7, it was shown that oxygen and hydrogen, uniting to form water, did so in the ratio of 1 volume of oxygen to 2 volumes of hydrogen, and that when water was decomposed it produced 1 volume of oxygen to 2 volumes of hydrogen. By weight, water consists of 88.88% oxygen and 11.11% hydrogen. Chemically pure water has a definite composition regardless of its source. Whether it is obtained from the melting of pure ice, from the condensation of steam, from the decomposition of a hydrate, or from the chemical union of hydrogen and oxygen gases, its composition is always the same. Here again a question arises, "Do all samples of any chemical compound always have the same composition?"

If mercuric oxide is selected as a representative compound, an experiment may be performed as illustrated in Fig. 9.2. A small amount of mercuric oxide is placed in a previously weighed pyrex test-tube, and the two weighed again and then heated to effect decomposition. When the decomposition is complete, the test-tube and contents are reweighed. Following are some observations from an actual experiment:

Weight of empty tube	12.250 gm.
Weight of tube and mercuric oxide	13.675 gm.
Weight of tube and mercury	13.570 gm.

Calculations:

Weight of mercuric oxide	1.425 gm.
Weight of mercury obtained	1.320 gm.

∴ weight of oxygen given off

(Law of Conservation of Mass) 0.105 gm.

∴ in 1.425 gm. of mercuric oxide there are 1.320 gm. of mercury and 0.105 gm. of oxygen.

$\therefore$ 100 gm. of the oxide would contain $\frac{100 \times 1.320}{1.425} = 92.63$ gm.

mercury and 7.37 gm. oxygen.

When the analysis is repeated a number of times with different samples of mercuric oxide, **in all cases** the percentage composition is found to be (within the limits of experimental error) 92.6% mercury and 7.4% oxygen. This ratio by weight never varies. Mercuric oxide has a fixed composition. Ten grams of pure mercuric oxide will always contain 9.26 grams of mercury and .74 grams of oxygen.

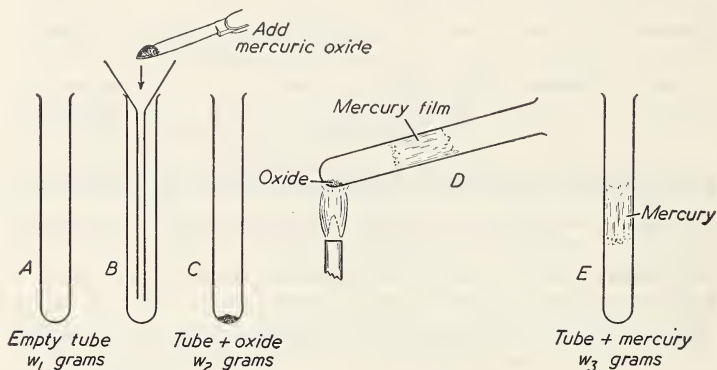


Fig. 9.2. The Law of Definite Proportions. The percentage composition by weight of mercuric oxide may be determined from this experiment.

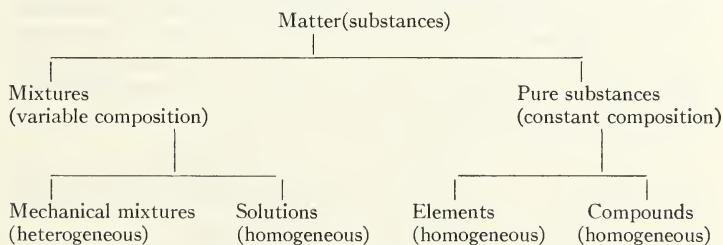
Common salt always contains sodium and chlorine in the ratio by weight of 23 parts of sodium to 35.5 parts of chlorine. Many other examples could be given and it always follows that the composition of a compound is fixed or definite. This is one of the most fundamental concepts of chemistry, and although first formulated by Dalton it may now be stated as a Law and called the **Law of Definite Proportions** or the **Law of Constant Composition**. *If all samples of a chemical compound be examined, the proportion by weight of the elements composing it will always be the same, or the percentage composition of a compound is fixed.* No circumstances whatever can alter the proportional quantities (by weight) of the constituents of a compound.

Man does not know why elements always unite in unvarying proportions. All that he knows is that the Creator has impressed this principle on matter to man's advantage. If elements did not unite in fixed and definite proportions, there would be no stability in either the

properties or composition of natural or man-prepared chemical substances, and what at one time might act as a medicine at another time could be a poison. This law is also of great importance to the chemical manufacturer. He knows that there is one proportion, and one only, in which the constituents of the compound he is manufacturing will react, and he makes conditions as perfect as possible to avoid all needless waste of materials.

Elements and compounds. Although prepared by various methods, a **pure substance** always has the same properties under a given set of conditions. Thus oxygen, hydrogen, water, mercury, mercuric oxide, potassium chlorate, and potassium chloride, are all pure substances. All pure substances can be classified as either elements or compounds. An **element** is a simple substance that has not been separated into simpler substances by ordinary chemical means, and that has never been formed by the union of simpler substances. Oxygen, hydrogen, and mercury are elements because, up to the present time, none of them has ever been broken down into two or more simpler substances by a simple chemical reaction. Water, mercuric oxide, potassium chlorate, and potassium chloride are **compounds**. Every compound is composed of at least two elements that are chemically united in a fixed and definite proportion by weight. The elements united in the compound are called the **constituents** of the compound. Thus the elements, oxygen and hydrogen, are the constituents of the compound, water. Both elements and compounds are homogeneous. In uniting to form a compound, the elements lose their identity. Thus water has quite a different "set" of properties from either oxygen or hydrogen.

A CLASSIFICATION OF SUBSTANCES



Mechanical mixtures. When a mixture of iron filings and flowers of sulphur is examined with a lens, the iron can easily be distinguished from the sulphur. A magnet passed through the mixture will remove the iron. When shaken with water, the iron sinks to the bottom quickly because it is denser than sulphur. When shaken with a sulphur solvent,

carbon disulphide, the sulphur dissolves, and the insoluble iron can be recovered by filtration. The sulphur and the iron in the mixture retain their original properties and can be separated from one another without a chemical change. If analyses were made from various samples of the mixture, they would show variations in the proportion by weight of iron and sulphur, thus indicating that a mechanical mixture is **heterogeneous**. The ingredients of a mixture are called the **phases** and are sometimes referred to as the **components**.

Mixtures are by far the most common of substances. In fact it is practically impossible to get an absolutely pure substance. The label on a bottle of a so-called chemically pure substance gives the percentage of impurities even though these percentages may be extremely small. In nature, pure substances are seldom found in any great quantity.

Examples of mechanical mixtures. Granite is a rock consisting of a mixture of three minerals, quartz, feldspar, and either mica or hornblende. River sands are mixtures. Those of the Yukon River contain gold that, because of its density, settles to the bottom of the sluice-box when the miner carries on his sand-washing operations. The mixture of clay and water referred to in Chapter 8, unlike a clear solution, is turbid. The solid phase can be separated from the liquid phase by filtration. The emulsions mentioned in Chapter 8 are examples of mixtures. Cream will separate from whole milk very slowly, but if the milk is whirled in a centrifuge the separation occurs more rapidly. Smoke is a mixture because it is a suspension of fine solid particles in air, and clouds and fog are suspensions of tiny drops of water in air. If the properties of the different phases in a mixture are known, it is usually a simple matter to separate them from one another.

Air is a mixture. Air was once regarded as an element. Later, when it was found that oxygen and nitrogen existed in approximately constant proportions in the atmosphere, some chemists suggested that air is a true chemical compound. However, the following reasons make clear the fact that air is a mixture and not a compound.

1. Although the composition of air is approximately constant, the slight variations existent are sufficient to prove that air is a mixture. The percentage composition of a compound is fixed.

2. When a gaseous compound is dissolved in water, its composition is not affected, so that if the gas is recovered by heating the water, no alteration in composition is found. When water, containing dissolved air, is heated and the air driven out and collected, the expelled air contains approximately one volume of oxygen to two volumes of nitrogen. In normal air, the ratio is approximately one to four.

3. If oxygen and nitrogen are mixed, no heat is evolved. No energy changes occur in the formation of a mixture.

4. In a mixture, the properties are additive. The properties of air are those of a mixture of nitrogen and oxygen, and each element retains its individual properties. Moreover, a mixture of nitrogen, oxygen, carbon dioxide, and water vapour in the same proportions in which these substances are found in air can be made, and it shows all the properties of air.

5. Air can be separated into its components by mechanical methods without a chemical reaction. This can be done by the fractional distillation of liquid air, or by making use of differences in diffusion of the components. Oxygen escapes through rubber more rapidly than does nitrogen, so that the gas in an automobile tire that has not been pumped up for a long time is mostly nitrogen. If oxygen and nitrogen were combined, they would pass through the rubber with equal velocities.

6. A formula cannot be written to express the accurate composition of air (see p. 119).

A SUMMARY OF MIXTURES, SOLUTIONS, AND COMPOUNDS

BASIS OF COMPARISON	MECHANICAL MIXTURES	SOLUTIONS	COMPOUNDS
Uniformity	Heterogeneous	Homogeneous	Homogeneous
Phases	2 or more	1	1
Changes in properties of components or constituents	None	Not permanently	Complete
Variations in proportions of components or constituents	No limit to variations	Variation within certain limits	No variation possible
Evolution of energy during preparation	None	Usually temperature drops, sometimes rises, e.g. sulphuric acid in water	Energy in some form always liberated or absorbed
Separation or recovery of components or constituents	Physical	Physical	Chemical only
Examples	Granite	Brine	Mercuric oxide

EXERCISE

A

1. (a) State the Law of Conservation of Mass (Law of Conservation of Weight). (b) Describe an experiment to illustrate this law, and include a labelled drawing of the apparatus used. (c) Recopy and complete the following word

equations: (i) Sodium chloride + Silver nitrate $\longrightarrow$ (ii) Potassium iodide + Lead nitrate $\longrightarrow$

2. (a) What is a precipitate? (b) Name the two precipitates produced in the reactions suggested in question 1 (c).

3. Distinguish between the terms mass and weight.

4. (a) State the Law of Definite Proportions (Law of Constant Composition). (b) Describe in detail how this law may be verified by experiments in which samples of mercuric oxide are heated. (Any other experiments you have performed in the laboratory to verify this law may be substituted.) (c) Show how the Law of Conservation of Mass is made use of in drawing conclusions from the experiments referred to in (b).

5. Give two reasons why the Law of Definite Proportions is of great importance to chemists.

6. (a) List four different methods of preparing samples of chemically pure water. (b) What statement can be made about the composition of these four samples?

7. When completely reduced by a current of dry hydrogen, 7.5 grams of cupric oxide gave 6.0 grams of metallic copper. When completely oxidized by heating in air, 4.5 grams of copper yielded 5.625 grams of cupric oxide. Show how these two experiments illustrate the Law of Definite Proportions.

8. Three samples of zinc oxide were prepared from metallic zinc by three different methods: (a) After being heated in the presence of a current of oxygen, 4.5 grams of zinc gave 5.607 grams of zinc oxide. (b) When 3 grams of zinc were heated in an atmosphere of steam, they gave 3.738 grams of zinc oxide. (c) Zinc nitrate was formed by completely dissolving 6 grams of zinc in nitric acid. This nitrate was then decomposed by intense heat and yielded 7.476 grams of zinc oxide. Show how these experiments illustrate the Law of Definite Proportions.

9. Define each of the following, and give an example in each case: pure substance, chemical element, chemical compound, homogeneous substance, heterogeneous substance, mechanical mixture, solution.

10. (a) Give five examples of elements that are solids, two that are liquids, and four that are gases at room temperature. (b) Give four examples of compounds that are solids, three that are liquids, and two that are gases at room temperature.

11. List of substances: pure water, granite, crude petroleum, dilute hydrochloric acid, brass, potassium chlorate, tincture of iodine, smoke, milk. From the above list select (a) those substances that have constant compositions, (b) those substances that are not chemical compounds. Give your reasons in each case.

12. (a) What mechanical methods of separation could be used to separate the phases in the following mixtures: (i) finely-divided iron from flowers of sulphur, (ii) white sugar from white aquarium sand, (iii) cream from milk, (iv) gold from gold-bearing river sands, (v) cod-liver oil from a cod-liver oil emulsion? (b) What physical properties are made use of in separating the phases of mixtures?

13. "Air is a mixture." Give five arguments that confirm this statement.

14. Summarize the chief differences between: (a) mechanical mixtures and compounds, (b) chemical compounds and solutions, (c) mechanical mixtures and solutions.

CHAPTER 10

The Gas Laws

Experimentally we do not know of any gas behaving in strict conformity to the law of Boyle; but in the case of many gases, and of nearly all gases at very high temperatures, the deviation from uniformity is very slight.

J. B. STALLO

Gases are easily compressed. Because of their relatively large intermolecular spaces, gases are more easily compressed than are the other states of matter. A smaller volume results as increased pressure on a gas forces the molecules closer together.

Gases exert pressure. Since molecules are in continuous motion, crowding them together into a smaller volume means a greater molecular bombardment per unit area on the walls of the container. A "more compact" gas, therefore, exerts a greater pressure than one in which the intermolecular spaces are larger. When air is removed from a bell jar as in Fig. 10.1, the jar cannot easily be lifted from its stand. The bombardment of the molecules of air outside the bell jar creates a pressure much greater than that produced by the few remaining molecules inside the jar. On the other hand, when air is admitted to the bell jar to such an extent that the molecular bombardment inside the jar equals that outside, the exertion of a force just great enough to overcome the weight of the bell jar is all that is necessary to remove it from the stand.

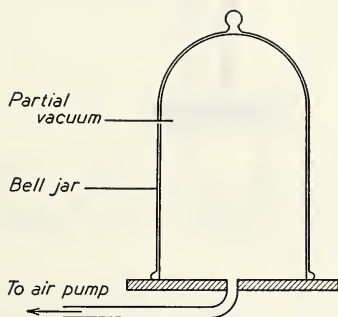


Fig. 10.1. Considerable force is required to remove the bell jar from the stand.

Measuring air pressure. In 1643, Torricelli invented an instrument for measuring air pressure. He took a glass tube about one metre long, closed at one end, and filled it with mercury (Fig. 10.2). Putting his finger over the open end, he placed the tube in a vertical, but inverted, position with the open end under the surface of the mercury in a dish, and then removed his finger. The mercury fell a short distance in the

tube and came to rest. The pressure exerted by the atmosphere on the surface of the mercury in the dish was sufficient to support some, but not all, of the mercury in the tube.

This apparatus for measuring air pressure is called a **barometer**, and the modern mercury barometer is the same in principle as that

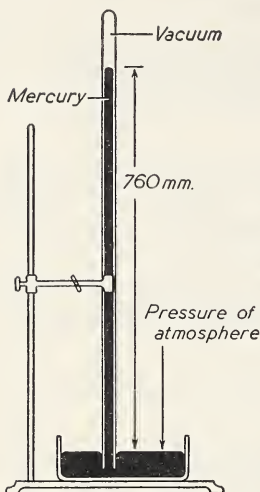


Fig. 10.2. A simple mercury barometer. Any change in the height of the column of mercury indicates a change in the pressure exerted by the atmosphere.

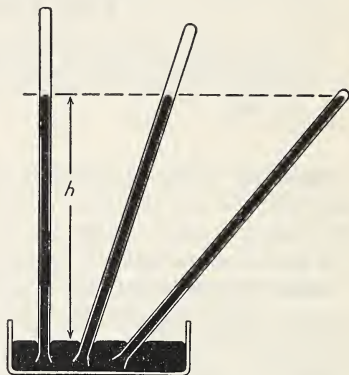


Fig. 10.3. If the barometer tube is inclined at different angles, the perpendicular height of the mercury column h remains the same.

constructed by Torricelli. Any change in the height of the column of mercury indicates a change in the pressure exerted by the atmosphere. The measurement of pressure involves units of force per unit area. A mass of 150 pounds exerts a force of 150 pounds weight, and if the area on which the force acts is 50 square inches, a pressure of 3 pounds per square inch is exerted.

If a barometer is inclined at different angles, as shown in Fig. 10.3, the mercury will rise in the tube, but the perpendicular distance h , measured between the mercury level in the dish and the level of the mercury in the tube, will not vary. This distance is used to express the value of the pressure exerted by the air. Thus when h measures 30 inches, the pressure of the atmosphere is equal to that exerted by a column of mercury 30 inches high. The statement, "The pressure is 30 inches," means that the air is pressing with sufficient force to support a column of mercury in a barometer tube to a height of 30 inches. The average pressure at sea level is 760 millimetres (76 cm.). This is

often referred to as a pressure of one atmosphere, or as **standard** or **normal pressure** and is approximately equal to a pressure of 15 pounds per square inch. If air is compressed, it can be made to exert pressures considerably greater than those encountered in nature. A pressure sufficient to support a column of mercury 152 cm. high is said to be a pressure of 2 atmospheres.

Boyle's Law. An increase of pressure on a gas decreases its volume. The exact relation between the volume of a given mass of gas and the pressure exerted upon it was first determined by Robert Boyle in 1662. Boyle was attempting to explain the various lengths of mercury columns in the Torricellian tube (barometer). He used a U-tube, sealed at one end as in Fig. 10.4, and poured in just enough mercury to fill the bend. By manipulating the tube, he was able to get the mercury to stand at the same height in both arms of the tube. Thus, he enclosed air in the short arm of the tube. This enclosed air was at the same pressure as the outside atmosphere, shown on the barometer to be 29 inches. Boyle then poured in mercury until he had reduced the volume of air in the short arm to one-half. On measuring the heights of the mercury in the two arms, he found that the mercury in the longer part of the tube was 29 inches higher than in the shorter arm. The pressure then had been increased from 29 inches to twice 29 inches: it had been doubled. It can be demonstrated

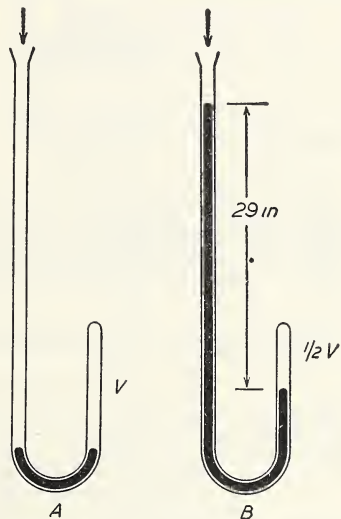


Fig. 10.4. A Boyle's Law tube. In A, a volume of gas V is enclosed in the closed arm of the bent tube. Because the mercury is at the same level in both arms, the pressure exerted on V is equal to atmospheric pressure (in this case assumed to be 29 in.). In B the mercury in the long arm is 29 in. higher than in the closed arm and the pressure exerted on the enclosed gas is 2×29 in. The volume is half the original volume.

experimentally that when the pressure is increased threefold, the volume of the enclosed air will be one-third; when increased fourfold, the volume is decreased to one-quarter; and so on. It should be noted that the temperature is kept constant during these experiments. Boyle's law states that *if the temperature is kept constant, the volume of a given*

mass of gas varies inversely as the pressure to which it is subjected.

Problem. If 500 cc. of oxygen are collected at a pressure of 740 mm., what would be the volume if the gas were collected at standard pressure, assuming no change in temperature?

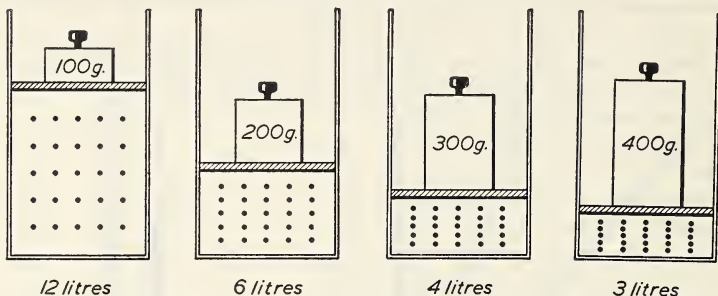


Fig. 10.5. Illustrating Boyle's Law. Each diagram represents the same mass of gas. When the pressure on the gas is doubled, the molecules are forced into half the space. When the pressure is tripled, the volume is one-third of the original volume. Increasing the pressure to four times the original pressure results in a volume one-quarter that of the original volume.

Solution. Since the new pressure is $\frac{760}{740}$ of the old pressure, and since the volume varies inversely as the pressure, the new volume must be $\frac{740}{760}$ of the former volume.

$$\therefore \text{the new volume } \frac{740}{760} \times 500 = 486.8 \text{ cc.}$$

Alternative solution. If V represents the original volume of a gas and P its original pressure, and V_1 and P_1 the new volume and pressure respectively, since one factor increases as the other decreases, the equation $\frac{V}{V_1} = \frac{P_1}{P}$ algebraically expresses Boyle's Law.

$$\text{Substituting, } \frac{500}{V_1} = \frac{760}{740}$$

$$\text{Whence } V_1 = 486.8 \text{ cc.}$$

Determining the coefficient of expansion of a gas. The increase in volume experienced by a unit volume of a gas when its temperature is raised one centigrade degree is called the **coefficient of expansion** of that gas. The following simple experiment determines the coefficient of expansion of air. The apparatus used consists of a 100 cc. flask,

300 cc. beaker, thermometer, retort stand, gauze, burner, one-hole stopper, short pieces of glass and rubber tubing, clamp, and a sheet metal cover with a semi-circular hole of suitable size to accommodate the neck of the flask.

Insert the short glass tube in the stopper and attach the piece of rubber tubing, making sure there are no leaks. Insert the rubber stopper in the empty flask and place the flask in about one inch of water in the bottom of the beaker. Cover the beaker and heat until the

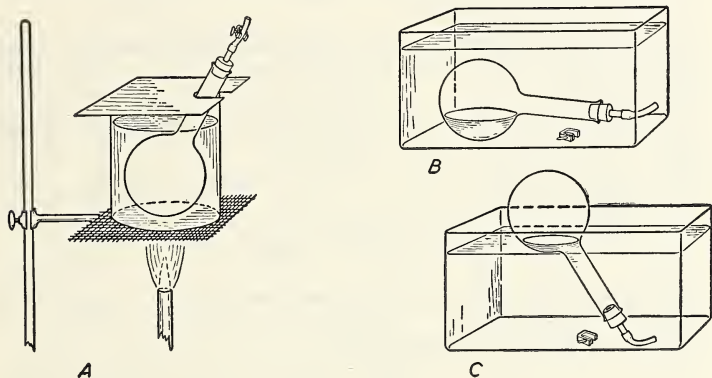


Fig. 10.6. *A*, a flask full of air is being heated in boiling water to approximately 100°C . *B*, the hot air has been cooled and has contracted. The contraction in volume is represented by the volume of water that has entered the flask. *C*, the water levels are adjusted so that the air in the flask is at atmospheric pressure.

water has been boiling about five minutes (Fig. 10.6 *A*). Now clamp the tube, thus enclosing a volume of hot air, and invert the flask in cold water in the sink or pneumatic trough. Make sure that the stopper and tube are kept covered with water. Remove the clamp and hold the flask under water to cool the air and until no more water enters it. Equalize the levels of the water inside and outside the flask to ensure that the air pressure inside is balanced by the atmospheric pressure outside (Fig. 10.6 *C*). Pinch the end of the tube under water, remove the flask, and turn it up to allow the trapped water in the tubing also to run into the flask. Remove the stopper and take the temperature inside the flask close to the water. Then pour the water into a graduate to find the volume of water that entered the flask. This volume obviously represents the "shrinkage" in volume when the flask full of hot air was cooled to the temperature of the water in the trough.

Fill the flask with water and insert the stopper to the same depth as before. Remove the stopper and find the volume of the water that fills the flask. This represents the total volume of hot air that was cooled.

During such an experiment, the following observations were made:

Temperature of boiling water		100° C. (appr.)
Temperature of air after cooling		14° C.
Volume of water entering flask		29 cc.
Volume of water filling flask		125 cc.

125 cc. of air at 100° C., cooling to 14° C., contracted 29 cc. Thus, if 96 cc. of air at 14° C. were heated to 100° C., they would exactly fill the flask.

96 cc. of air at 14° C., heated through 86 centigrade degrees, expand 29 cc.

1 cc. of air, heated through 1 centigrade degree, expands

$$\frac{1}{96} \times \frac{1}{86} \times 29 = \frac{1}{284} \text{ cc.}$$

Therefore, the coefficient of expansion of air at 14° C. = $\frac{1}{284}$, and at 0° C. the coefficient of expansion is

$$\frac{1}{284 - 14} = \frac{1}{270}.$$

The reason for this difference in coefficient at 0° C. and 14° C. will be considered later. From accurate experiments the coefficient of expansion of air at 0° C. has been found to be $\frac{1}{273}$.

Experiments with many different gases have shown that *all gases have this same coefficient*.

Coefficients at various temperatures. Suppose at a pressure of 760 mm. and a temperature of 0° C. a small pellet of mercury encloses a column of air exactly 273 cm. long in a glass tube with a cross-sectional area of 1 sq. cm. as shown in Fig. 10.8. Thus the pellet encloses 273 cc. of air at 0° C. in the tube. Imagine the temperature to increase to 1° C. Since 1 cc. of any gas, heated from 0° C. to 1° C., expands $\frac{1}{273}$ cc., it follows that 273 cc., heated from 0° C. to 1° C., expand $273 \times \frac{1}{273} = 1$ cc., and the new volume would be 274 cc.

Similarly 273 cc., heated from 0°C. to 10°C. , would become 283 cc.; and 273 cc. at 0°C. , heated to 11°C. , would become 284 cc.

Next, consider the 283 cc. at 10°C. being heated to 11°C. The volume, of course, becomes 284 cc. Hence 283 cc. at 10°C. , heated 1 centigrade degree, expand 1 cc.; and 1 cc. at 10°C. , heated 1 centigrade degree, expands $\frac{1}{283}$ cc., and

the coefficient at 10°C. is $\frac{1}{283}$.

Similarly the coefficients at 15°C. , 20°C. , and 30°C. , are $\frac{1}{288}$, $\frac{1}{293}$, and $\frac{1}{303}$, respectively.

Therefore, at any temperature the coefficient is:

$$\frac{1}{273 + \text{temperature (in centigrade)}}.$$

Absolute zero. At -10°C. the original 273 cc. of gas at 0°C. would occupy 263 cc. and at -100°C. its volume would be 173 cc. and the coefficients would be

$$\frac{1}{273 + (-10)} = \frac{1}{263} \text{ and}$$

$$\frac{1}{273 + (-100)} = \frac{1}{173}, \text{ respectively.}$$

Theoretically at -273°C. the volume of the original 273 cc. would be zero, i.e. the gas would have lost all its volume. In reality, all gases liquefy before this temperature is reached and, of course, the gas laws cease to apply. At -273°C. all molecular motion would cease and the substances would be without any heat and would be absolutely cold. Thus -273°C. is said to be the **absolute zero** because, at this temperature, a body would be incapable of losing heat.

Absolute temperature. In comparing gas volumes, Lord Kelvin devised the absolute temperature scale to overcome the difficulty presented by minus readings on the thermometer. Minus 273°C. , was chosen as absolute zero and the divisions chosen were the same in

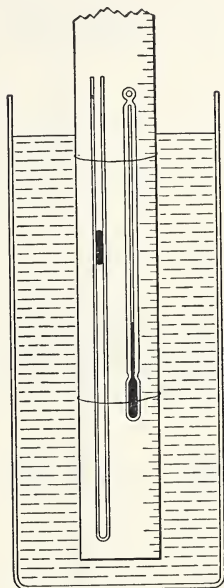


Fig. 10.7. A Charles's Law tube. A volume of air is enclosed in a tube by a mercury pellet. The temperature of the water bath in which the tube is immersed can be regulated; the thermometer indicates each temperature.

CHARLES'S LAW

CENTIGRADE TEMPERATURES	VOLUME	ABSOLUTE TEMPERATURES
0° C.	273 cc.	273° A.
1° C.	274 cc.	274° A.
10° C.	283 cc.	283° A.
11° C.	284 cc.	284° A.
273° C.	546 cc.	546° A.
-10° C.	263 cc.	263° A.

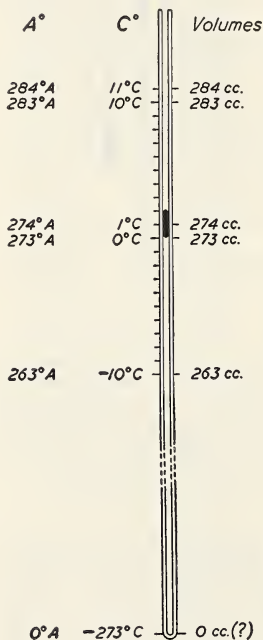


Fig. 10.8. Diagram showing the relationship between the volumes and absolute temperatures of a gas. Note that if the original volume is 273 cc. at 0°C., the numerical values of both volume and absolute temperature are the same for each temperature.

size as those on the centigrade scale. To change any centigrade reading (C.) to the corresponding absolute reading (A.), 273 is added to the centigrade reading (Fig. 10.8). Thermometers are not made with the graduations marked in absolute. The absolute scale is merely a convenience arbitrarily devised to simplify calculations in comparing gas volumes.

Charles's Law. The tube of air shown in Fig. 10.8 could be used as a thermometer. If the original volume used was 273 cc. at 0° C., the volumes in cubic centimetres and the temperatures on the absolute scale would be numerically equal.

The above table indicates that the volume is doubled if the absolute temperature is doubled. If the absolute temperature is made $\frac{283}{273}$ $\times$ the original temperature,

the volume becomes $\frac{283}{273}$ $\times$ the original volume. If the absolute temperature is made $\frac{263}{283}$ $\times$ the original temperature, the

volume becomes $\frac{263}{283}$ $\times$ the original volume. This relationship can be expressed mathematically by saying that the volume of a gas varies directly as the absolute

temperature. This is only true provided that no change in pressure occurs.

If the pressure is kept constant, the volume of a given mass of gas varies directly as the absolute temperature. This is known as Charles's Law.

Problem. If 3 litres of oxygen were collected at $20^{\circ}\text{C}.$, what would its volume be at $30^{\circ}\text{C}.$ (pressure unchanged)?

Solution. $20^{\circ}\text{C.} = 293^{\circ}\text{A.}$, and $30^{\circ}\text{C.} = 303^{\circ}\text{A.}$ The new temperature is greater, therefore the volume will be greater.

Form an "increasing fraction" with the absolute temperatures thus, $\frac{303}{293}$. The gas will expand to $\frac{303}{293}$ of its former volume.

New volume $\frac{303}{293} \times 3 = 3.102$ litres.

Alternative solution. If V and T represent the original volume and temperature (absolute) of a gas, and V_1 and T_1 the new volume and temperature (absolute), then Charles's Law can be expressed algebraically:

$$\frac{V}{V_1} = \frac{T}{T_1}$$

$$\text{Substituting, } \frac{3}{V_1} = \frac{293}{303}$$

Whence $V_1 = 3.102$ litres.

Standard temperature. Often, when a gas is collected in a laboratory, both the temperature and pressure conditions at which it is measured are noted. These conditions would have to be the same for a comparison of volumes of the gas so collected to have significance. The temperature often selected for this comparison is 0°C. , or 273°A. This temperature is called **standard**, or **normal**, **temperature**. Hence 0°C. and 760 mm. are called standard temperature and standard pressure respectively. This is often abbreviated to **S.T.P.**

Problem. 200 cc. of hydrogen were collected at 18°C. when the barometer pressure was 740 mm. What volume would the hydrogen occupy at S.T.P.?

Solution.

	Volume	Pressure	Temperature
Original conditions	200 cc.	740 mm.	$273 + 18 = 291^{\circ}\text{A.}$
New conditions	?	760 mm.	$273 + 0 = 273^{\circ}\text{A.}$

Assuming for the moment that the temperature did not change, let us consider only the effect of the change of pressure on the given volume.

The pressure has been increased, therefore the volume will be decreased. Applying Boyle's Law, the new volume $= \frac{740}{760} \times 200$ cc.

Now let us consider the effect of the change in temperature cited in the problem on such a volume of gas, i.e. on $\left(\frac{740}{760} \times 200\right)$ cc.

The temperature has been decreased, therefore the volume will be decreased. Applying Charles's Law, the new volume is

$$\frac{273}{291} \times \left(\frac{740}{760} \times 200\right) = 182.7 \text{ cc.}$$

Alternative solution. The following formula may be used to solve problems involving simultaneous pressure and temperature changes:

$$\frac{PV}{T} = \frac{P_1V_1}{T_1}$$

where P, V , and T represent the original pressure, volume, and absolute temperature respectively, and P_1, V_1 , and T_1 represent the new pressure, volume and absolute temperature.

$$\text{Substituting, } \frac{740 \times 200}{291} = \frac{760 \times V_1}{273}$$

$$\text{Whence } V_1 = 182.7 \text{ cc.}$$

EXERCISE

A

1. What conditions produce changes in the volumes of gases, and what are the effects produced?
2. Why is it necessary to have standard conditions of temperature and pressure?
3. What are the standard conditions used in measuring the volumes of gases?
4. (a) State Boyle's Law. (b) State Charles's Law.
5. Is it possible to have changes in both pressure and temperature that would cause the volume of a gas to remain unchanged?
6. What is assumed when one makes the statement "1 litre of hydrogen weighs 0.0898 grams"? Why?

B

1. A sample of helium occupies a volume of 400 cc. under a pressure of 752 mm. If the pressure becomes 700 mm., find the new volume.

2. Calculate the volumes which would be occupied at the given final pressures by the gases whose initial volumes and pressures are listed below. Assume in each case that the temperature remains constant.

<i>Initial Volume</i>	<i>Initial Pressure</i>	<i>Final Pressure</i>
(a) 245 cc.	740 mm.	760 mm.
(b) 450 cc.	760 mm.	730 mm.
(c) 4.16 litres	758 mm.	Standard pressure
(d) 63.3 litres	74.2 cm.	76 cm.
(e) 3.06 cu. ft.	1 atmosphere	1.25 atmospheres

3. (a) How are Centigrade temperatures converted to the corresponding Absolute scale readings? (b) Convert the following Centigrade readings to the corresponding reading on the Absolute scale: 0°C. ; 20°C. ; 73°C. ; -20°C. ; -273°C.

4. A given mass of gas occupies 160 cc. at 20°C. What volume will it occupy at 100°C. if the pressure remains constant?

5. Calculate the volumes which would be occupied at the given final temperatures by the gases whose initial volumes and temperatures are listed below. Assume in each case that the pressure remains constant.

<i>Initial Volume</i>	<i>Initial Temperature</i>	<i>Final Temperature</i>
(a) 800 cc.	0°C.	27°C.
(b) 5.6 litres	15°C.	273°C.
(c) 635 cc.	22°C.	0°C.
(d) 25 litres	-15°C.	S.T.
(e) 190 cc.	S. T.	127°C.

6. Changes in volume most commonly occur because of simultaneous changes in temperature and pressure. A quantity of gas collected at 15°C. and 765 mm. pressure occupies 170 cc. What will be the volume of this gas at S. T. P.?

7. Calculate the volumes which would be occupied at the given final temperatures and pressures by the gases whose initial volumes, temperatures, and pressures are listed below.

<i>Initial Volume</i>	<i>Initial (T) and (P)</i>	<i>Final (T) and (P)</i>
(a) 144 cc.	0°C. and 760 mm.	18°C. and 770 mm.
(b) 1520 cc.	0°C. and 738 mm.	-27°C. and 735 mm.
(c) 22.4 litres	S. T. P.	15°C. and 800 mm.
(d) 22400 cc.	120°C. and 722 mm.	S. T. P.
(e) 4 cu. ft.	-37°C. and 74.2 cm.	273°C. and 76 cm.
(f) 228 cc.	91°C. and 865 mm.	S. T. P.

8. Under standard conditions of temperature and pressure, 1 litre of oxygen weighs 1.43 gm. Find the weight of one litre of oxygen measured at 22°C. and 770 mm. pressure.

9. If 22.4 litres of sulphur dioxide gas weigh 64 grams at S. T. P., find the weight of 500 cc. of this gas which has been collected at 45°C. and 758 mm. pressure.

CHAPTER 11

Laws and Theories of Chemical Combination

The world is not a meaningless medley. We do not believe that blind chance reigns supreme. On the contrary, we see order everywhere, and law is the regulating principle in all things and processes.

P. CARUS

Equivalent and combining weights. According to the Law of Definite Proportions, every sample of a given compound consists of the same elements in the same ratio by weight. To learn more about the combination of the elements, let us examine some of the compounds formed by the union of various elements with oxygen. Oxygen is selected because it unites with most of the other elements.

Following is a list of these compounds with their percentage compositions by weight as determined by chemical analyses.

PERCENTAGE COMPOSITION BY WEIGHT OF OXYGEN COMPOUNDS

COMPOUND	OXYGEN (% by weight)	OTHER ELEMENT (% by weight)
Water	88.88	11.11 hydrogen
Carbon dioxide	72.73	27.27 carbon
Chlorine monoxide	18.39	81.61 chlorine
Mercuric oxide	7.40	92.60 mercury
Calcium oxide	28.57	71.43 calcium
Magnesium oxide	39.60	60.40 magnesium
Sodium oxide	25.81	74.19 sodium
Cupric oxide	20.10	79.90 copper

This "percentage" method is commonly used to show the proportion by weight in which the elements unite in various compounds. If 8 units by weight of oxygen are selected as a **combining weight** of oxygen, the weights of the other elements that will combine with this chosen weight of oxygen to form the several oxygen compounds listed may be calculated.

PROPORTIONATE COMPOSITION OF OXYGEN COMPOUNDS

COMPOUND	OXYGEN (proportion by weight)	OTHER ELEMENTS (proportion by weight)
Water	8 units	1 unit of hydrogen
Carbon dioxide	8 units	3 units of carbon
Chlorine monoxide	8 units	35.5 units of chlorine
Mercuric oxide	8 units	100 units of mercury
Calcium oxide	8 units	20 units of calcium
Magnesium oxide	8 units	12.12 units of magnesium
Sodium oxide	8 units	23 units of sodium
Cupric oxide	8 units	31.8 units of copper

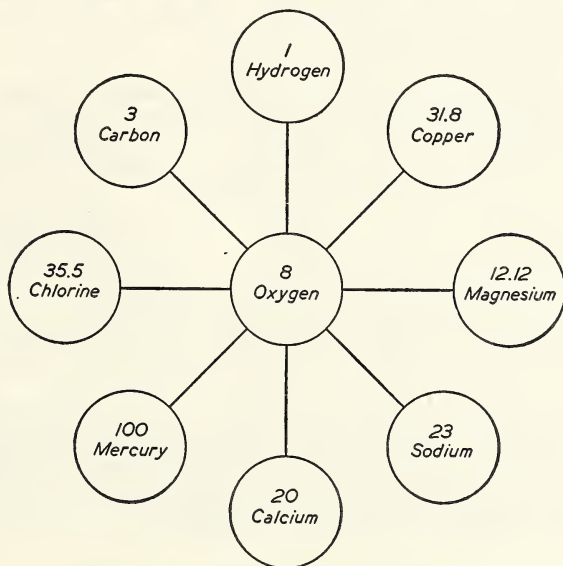


Fig. 11.1. Equivalent weights. The weights in any units of weight of several elements that will unite with eight of the same units by weight of oxygen.

There is nothing unusual in these numbers or quantities. The statements "Water is 88.88% oxygen and 11.11% hydrogen" and "8 units by weight of oxygen are united with 1 unit by weight of hydrogen to form 9 units by weight of water" have exactly the same meaning.

In the same way, analyses of a few compounds containing hydrogen as the common constituent show percentage by weight compositions as follows:

PERCENTAGE COMPOSITION BY WEIGHT OF HYDROGEN COMPOUNDS

COMPOUND	HYDROGEN (% by weight)	OTHER ELEMENT (% by weight)
Water	11.11	88.88 oxygen
Hydrogen chloride . .	2.74	97.26 chlorine
Methane	25.00	75.00 carbon
Sodium hydride . . .	4.17	95.83 sodium

As with oxygen, a combining weight can be assigned to hydrogen and the proper proportion of other elements expressed in terms of units in proportion to this combining weight. Thus, if 1 unit of hydrogen is selected as a combining weight, the facts presented in the above table may be expressed as follows:

PROPORTIONATE COMPOSITION OF HYDROGEN COMPOUNDS

COMPOUND	HYDROGEN (proportion by weight)	OTHER ELEMENTS (proportion by weight)
Water	1 unit	8 units of oxygen
Hydrogen chloride . .	1 unit	35.5 units of chlorine
Methane	1 unit	3 units of carbon
Sodium hydride . . .	1 unit	23 units of sodium

A comparison of the above tabulations brings to light a surprising fact. Evidently the weights of the various elements that unite with 8 units by weight of oxygen to form oxides are the same weights that unite with 1 unit by weight of hydrogen to form hydrides.

A single table may show both the percentage composition by weight and the number of units by weight of other elements that will combine with a stated combining weight of a given element. For example, assuming a combining weight of 35.5 for chlorine, the composition of chlorine compounds may be shown as follows:

COMPOSITION OF CHLORINE COMPOUNDS

CHLORIDES	CHLORINE (% by weight)	OTHER ELEMENT (% by weight)	UNITS BY WEIGHT UNITING WITH 35.5 UNITS BY WEIGHT OF CHLORINE
Mercuric chloride	26.30	73.70 mercury	100 units of mercury
Sodium chloride	60.70	39.30 sodium	23 units of sodium
Chlorine monoxide	81.61	18.39 oxygen	8 units of oxygen
Hydrogen chloride	97.26	2.74 hydrogen	1 unit of hydrogen
Cupric chloride	52.70	47.30 copper	31.8 units of copper
Carbon tetrachloride	92.20	7.80 carbon	3 units of carbon

The above table shows that the weights of the various elements that united with 35.5 units by weight of chlorine are the *same weights*

found united with 8 units by weight of oxygen and 1 unit by weight of hydrogen.

If the *gram* is selected as the unit of weight, these amazing relationships can be represented graphically as follows:

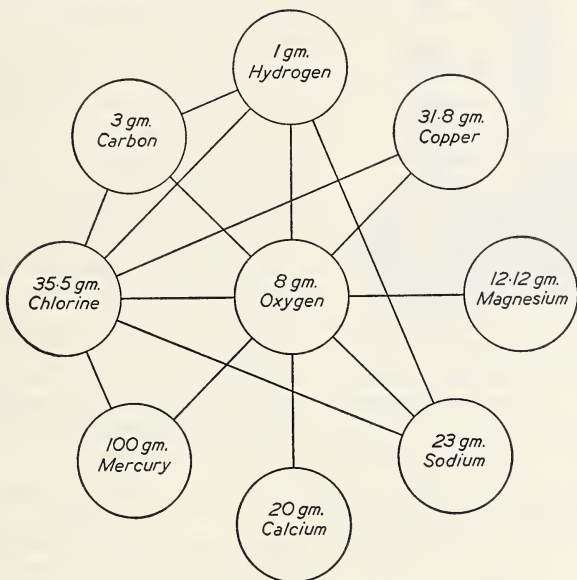


Fig. 11.2. Gram-equivalent weights of nine elements. When the elements react among themselves they do so in proportion to these weights. If the elements were parcelled as shown, and if a reaction took place between any two of them, they would react so that each parcel would be used up completely. Thus 12.12 gm. magnesium would unite completely with 35.5 gm. chlorine to form 47.62 gm. magnesium chloride. (N.B. Sometimes the elements react in proportion to some simple multiple of these weights.)

Every element, with the exception of a few inert elements, has been made to unite with some other elements, but never with all. It should not be concluded that such union is impossible. All that can be said is that this has not yet been accomplished, possibly because the proper conditions for union have not been discovered to date. Magnesium and calcium, for example, do not combine, but 12.12 gm. of magnesium and 20 gm. of calcium will each liberate 1 gm. of hydrogen from certain compounds. If magnesium and calcium were made to unite under some as yet unknown conditions, it would be reasonable to conclude that they would do so in the proportion of 12.12 gm. to 20 gm., respectively.

The weights just established are called **gram-equivalent weights**, and the numbers represent the proportions in which these elements would either combine with one another or would replace one another. Thus, if the various elements were weighed out in the parcels shown in Fig. 11.2 in any units of weight (grams, pounds, ounces, tons, etc.), and if they reacted at all they would unite completely, nothing being left over. What is true for the equivalent weights of the elements selected here is true for the equivalent weights of all elements. *The equivalent weight of an element could be defined as the weight of that element that will combine with or displace 8 units by weight of oxygen, or the equivalent weight of any other element.* To illustrate, the equivalent weight of chlorine is 35.5, of carbon 3, of copper 31.8, and of hydrogen 1.

Law of Combining Weights. This scheme of equivalent weights is not really as simple as has been shown. The compounds used for illustration were selected to avoid confusion. However, it is not unusual for the same two elements to unite to form more than one compound. Therefore, some elements have more than one "combining" weight. For example, carbon and oxygen form two compounds, carbon dioxide and carbon monoxide. In carbon dioxide, 8 gm. of oxygen are combined with 3 gm. of carbon; but in carbon monoxide, 8 gm. of oxygen are combined with 6 gm. of carbon. In mercuric and mercurous oxides, two quite different oxides of mercury, 8 gm. of oxygen are combined with 100 gm. and 200 gm. of mercury, respectively. Thus carbon and mercury have at least two combining weights. The simplest combining weights found (those selected in the preliminary discussion) are the equivalent weights. *When elements combine to form compounds, they do so in proportion to some simple multiple of their equivalent weights.*

When 8 gm. of oxygen unite with 1 gm. of hydrogen, 9 gm. of water are formed; and when 8 gm. of oxygen unite with 20 gm. of calcium, 28 gm. of calcium oxide result. When calcium oxide reacts with water, the proportion by weight of the two compounds is 28 to 9, respectively. Therefore, 9 is an equivalent weight of water, and 28 an equivalent weight of calcium oxide. Compounds, as well as elements, have both equivalent weights and combining weights.

For each pure substance (both elements and compounds), a weight may be selected such that when these substances enter into chemical reaction they do so in proportion to these weights, or some simple multiple of them. This is known as the **Law of Combining Weights**.

Law of Multiple Proportions. The composition of carbon dioxide and carbon monoxide illustrate the Law of Multiple Proportions. In these two compounds, 8 units by weight of oxygen are united with

3 and 6 units by weight of carbon, respectively. These weights of carbon are in the simple ratio of 1 to 2. In mercuric and mercurous oxides, 8 units by weight of oxygen are united with 100 and 200 units by weight of mercury, respectively. These numbers are also in the simple ratio of 1 to 2. It is evident that elements may unite in more than one proportion to form a corresponding number of compounds. When they do, *if a fixed weight of one of the elements be chosen, then the different weights of the other element which unite with this fixed weight, will always bear a simple relationship to each other, i.e. a ratio of small whole numbers.* John Dalton first enunciated this law in 1803.



Fig. 11.3. Joseph Louis Gay-Lussac (1778-1850) formulated the Law of Gaseous Volumes.

Another example serves to illustrate this important law. Iron and chlorine form two compounds, ferrous and ferric chloride.

1. Ferrous chloride 44.09% iron; 55.91% chlorine
2. Ferric chloride 34.46% iron; 65.54% chlorine

If a fixed weight of iron is chosen, say 44.09 gm.:

In (1) 44.09 gm. iron are united with 55.91 gm. chlorine,

In (2) 44.09 gm. iron are united with $\frac{44.09}{34.46} \times 65.54 = 83.85$ gm. chlorine.

These weights of chlorine, 55.91 and 83.85 are in the ratio of 2 to 3, and this ratio conforms to the law.

Gay-Lussac's Law of Volumes. While Dalton was developing the Laws of Definite and Multiple Proportions, a French contemporary, Joseph Louis Gay-Lussac, was carrying out researches with gases. Whereas Dalton was concerned with combination by weight, Gay-Lussac was interested in combination by volume. In 1781, Cavendish had discovered that when hydrogen and oxygen combine they do so in the ratio of approximately 2 to 1 by volume. This discovery intrigued Gay-Lussac into investigating the volume relationships in other gaseous reactions. He found that:

- (a) 1 volume of hydrogen + 1 volume of chlorine $\longrightarrow$ 2 volumes of hydrogen chloride

- (b) 1 volume of nitrogen + 3 volumes of hydrogen $\longrightarrow$ 2 volumes of ammonia
- (c) 1 volume of oxygen + 2 volumes of carbon monoxide $\longrightarrow$ 2 volumes of carbon dioxide
- (d) 1 volume of oxygen + 2 volumes of hydrogen $\longrightarrow$ 2 volumes of steam

All volumes were measured under corresponding conditions of temperature and pressure. Gay-Lussac's investigations led him to formulate the following law known as the **Law of Gaseous Volumes** or **Gay-Lussac's Law of Volumes**: *When gaseous pure substances react, they do so in volumes bearing a simple ratio to one another and to the volumes of the products (if these are gases).*

Dalton's atomic theory. To explain the reason for the Law of Conservation of Mass, in 1803 Dalton devised the *chemical atomic hypothesis*. He made the following assumptions:

1. Matter is composed of small particles, or atoms, that cannot be subdivided by any known chemical process.
2. Atoms are indestructible and cannot be created. They do not divide when taking part in a chemical reaction.
3. Atoms of the same element are alike in all respects, including weight, and are different from atoms of other elements.
4. Atoms possess the power to attract or to hold on to other atoms.
5. Compounds are formed by the union of atoms of different elements.
6. The "atoms" of a compound are all alike and these "compound atoms" are formed by the combination of atoms of different kinds.

Dalton's fundamental ideas were expressed in such a way that they became an accepted working hypothesis. This hypothesis met with such success it has since been elevated to the position of a **theory**. Not only did the theory explain the reason for the Law of Conservation of Mass but Dalton was also able to use it to *predict* the Law of Definite Proportions and the Law of Multiple Proportions. He later verified both laws by experimental methods. The great value of a theory lies in the fact that it enables the scientist to predict what will happen in new and as yet untried situations. The **atomic theory** has been a great stimulus to the development of chemistry. Although modern chemists have been forced to modify Dalton's concepts, there is scarcely any other law or theory that has equally influenced scientific thinking or led to so many discoveries.

Gram-molecular weight (G.M.W.). It is interesting at this point to compare the proportions in which substances react by weight and by volume. The following list gives the gram-equivalent weights of a

few pure gaseous substances and also the volume that each gram-equivalent weight occupies at S.T.P.

GRAM-EQUIVALENT WEIGHTS	VOLUME OCCUPIED AT S.T.P.
8 gm. oxygen	5.6 litres
1 gm. hydrogen	11.2 litres
11 gm. carbon dioxide	5.6 litres
14 gm. carbon monoxide	11.2 litres
4 gm. methane	5.6 litres
35.5 gm. chlorine	11.2 litres
36.5 gm. hydrogen chloride	22.4 litres
43.5 gm. chlorine monoxide	11.2 litres

Only three volumes, 5.6 litres, 11.2 litres, and 22.4 litres, are found in the above list. The gram-equivalent weights of all gaseous pure substances, if listed, would occupy one of these three volumes at S.T.P.

It will be recalled that pure substances react in proportion to their combining weights. Therefore, if a chemical reaction were to take place between oxygen and carbon monoxide, for example, the proportion by weight of these reacting gases (according to the preceding table) would be in the ratio of some simple multiple of 8 to some simple multiple of 14. The proportion by volume would be some multiple of 5.6 litres of oxygen to some multiple of 11.2 litres of carbon monoxide. Although Gay-Lussac developed the Law of Volumes by actual experiments, it can readily be seen that because 5.6, 11.2, and 22.4 litres (S.T.P.) are the only volumes occupied by the gram-equivalent weights of all gases, they must react in volumes bearing a simple ratio to one another.

For comparative purposes, it is advantageous to select combining weights that would occupy the same volume. Since 22.4 litres at S.T.P. is the smallest volume that could contain the gram-equivalent weights of all gaseous pure substances, it is selected as the standard of volume

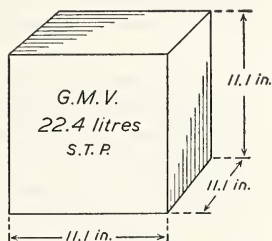


Fig. 11.4. The gram-molecular volume. This is the smallest volume that will contain the gram-equivalent weight of any pure gaseous substance measured at 0°C. and 760 mm. pressure.

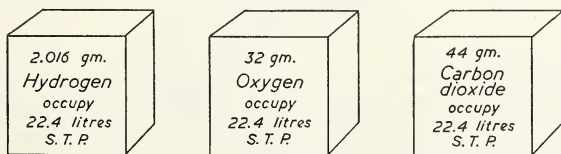


Fig. 11.5. Relation between gram-molecular volume and gram-molecular weight. The gram-molecular weight is the weight in grams of 22.4 l. of any gaseous pure substance measured at S.T.P.

and is known as the **gram-molecular volume**. The weight in grams of a gaseous pure substance that will fill this volume is called the **gram-molecular weight**. Hence the gram-molecular weights of the gases listed above are: oxygen 32 gm., hydrogen 2 gm., carbon dioxide 44 gm., carbon monoxide 28 gm., methane 16 gm., chlorine 71 gm., hydrogen chloride 36.5 gm., and chlorine monoxide 87 gm.

Gram-molecular weights of liquids. The gram-molecular weights of pure substances that are liquids at S.T.P. can be determined by a comparison with the gram-molecular weight of oxygen, provided the liquids can be vaporized without decomposition.

If 22.4 litres of oxygen at S.T.P. are heated (keeping the pressure constant) until its temperature is 100° C., the volume will increase to

$$22.4 \times \frac{373}{273} \text{ litres (Charles's Law)}$$

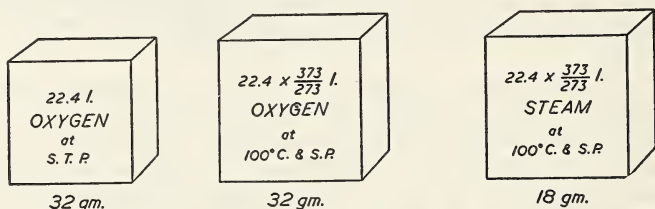


Fig. 11.6. Finding the gram-molecular weight of water which is not a gas at ordinary temperatures and pressures. The gram-molecular weight of water is 18 grams because this is the weight of steam (in grams) that will occupy the same volume as that occupied by 32 grams of oxygen at 100°C. and standard pressure.

This oxygen will still weigh 32 gm. Since all gases have exactly the same coefficient of expansion, 22.4 litres of *any* gas at S.T.P. would occupy

$$22.4 \times \frac{373}{273} \text{ litres at } 100^\circ \text{ C.}$$

To find the gram-molecular weight of water, this volume,

$$22.4 \times \frac{373}{273} \text{ litres,}$$

can be filled with steam at 100° C. and 760 mm. pressure, and weighed. This weight, which is found to be 18 gm., is the gram-molecular weight of water, for if the steam, when cooled to 0° C., could remain gaseous its volume would be 22.4 litres.

The gram-molecular weights of many liquids can be found in a similar manner. Note, however, that the liquid must be made gaseous

and that the gram-molecular weight is the weight of a certain volume of a gas. *Gram-molecular weight can be defined as the weight of a substance in the form of a gas at any temperature and pressure that will occupy the same volume as that occupied by 32 gm. of oxygen at the same temperature and pressure.*

Avogadro's Theory. The uniformities in the behaviour of gases led an Italian scientist, Amedeo Avogadro, in 1811, to enunciate the following hypothesis, later known as Avogadro's Theory. *Equal volumes of all gases at the same temperature and pressure contain the same number of molecules.* Avogadro was forced to introduce this new word **molecule** to overcome misconceptions that had arisen through trying to visualize Dalton's "compound atom". Avogadro recognized two kinds of ultimate particles, atoms and molecules. The smallest particle that can exist in a free state (e.g. the smallest particle of hydrogen or of hydrogen chloride) is called a **molecule**. The smallest particle capable of taking part in a chemical reaction, or that can be transferred from one chemical substance to another (e.g. the hydrogen or chlorine *contained in* a molecule of hydrogen chloride), is called an **atom**.

We can get a better picture of Avogadro's "particles" by representing a simple reaction graphically.



Fig. 11.7. Amedeo Avogadro (1776-1856).

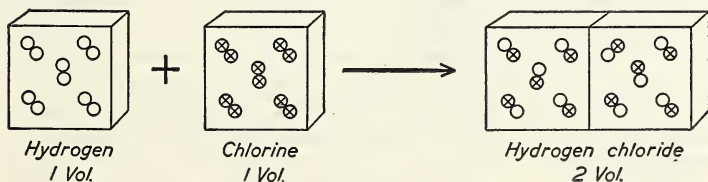


Fig. 11.8. The diagram represents five molecules of hydrogen (each molecule made up of two atoms) reacting with five molecules of chlorine (each molecule made up of two atoms), to form ten molecules of hydrogen chloride (each molecule containing one atom of hydrogen and one atom of chlorine).

Similarly the combination of hydrogen and oxygen may be represented as follows:

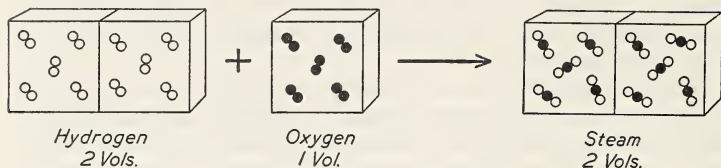


Fig. 11.9. The diagram illustrates why two volumes of hydrogen unite with one volume of oxygen to form two volumes of steam.

When molecules are separated into atoms and the atoms regrouped, a chemical change takes place. Molecules of elements are made up of atoms that are alike. Every compound contains at least two *kinds* of atoms in each molecule. As there are nearly 100 elements known, there are nearly 100 kinds of atoms.

Molecules can be compared to houses, and atoms to bricks. In ordinary chemical reactions the "houses" can be broken down but the "bricks" are indivisible. All chemical action takes place between the atoms.

The decomposition of water can be represented graphically:

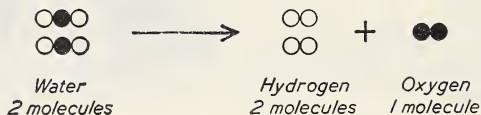


Fig. 11.10. In the diagram each molecule of water is made up of two atoms of hydrogen and one atom of oxygen. When water is decomposed, the atoms are not destroyed or changed in any way but are merely rearranged to form new substances.

Two molecules of water, each consisting of three atoms (2 of hydrogen and 1 of oxygen) change to form 3 molecules (2 of hydrogen and 1 of oxygen). Each molecule of hydrogen contains 2 identical atoms, and the molecule of oxygen contains 2 identical atoms of oxygen. Note that in the chemical reaction illustrated, there has been no change in the number of "bricks". *Elements pass into or out of combination without loss or gain in weight because the atom is not divided by chemical reaction.*

In 1860, a congress at Karlsruhe tried to clarify the confusion that had arisen through a misunderstanding of the terms "atom" and "molecule". Chemists spoke of "atoms of water" in the same way in which they spoke of "atoms of hydrogen". Avogadro had died in 1856,

but another great Italian scientist, Stanislao Cannizzaro (1826-1910), championed his cause so successfully that the congress adopted Avogadro's ideas.

Recent investigators have been able to calculate the number of molecules in a given volume of gas and have found that 22.4 litres of every gas at S.T.P. contain 6.02×10^{23} molecules. This is known as *Avogadro's number*.

Molecular weight. The volumes shown in Fig. 11.5 are equal, but the ratio of the weights are 2 to 32 to 44. If these equal volumes contain the same number of molecules, it is evident that if x molecules of oxygen weigh 32 gm., then x molecules of hydrogen weigh 2 gm., and x molecules of carbon dioxide weigh 44 gm. Therefore a single

molecule of carbon dioxide is $\frac{44}{32}$ times as heavy as a single molecule of

oxygen, and a single molecule of hydrogen is $\frac{2}{32}$ times as heavy as a

single molecule of oxygen. Hence the numbers, 32, 2, and 44 represent the **relative weights** of the individual molecules, and these *numbers* (based on oxygen = 32) are called **molecular weights**. There are other more complex methods of comparing molecular weights too difficult for discussion at this time. It should be emphasized that molecular weights are relative numbers, whereas gram-molecular weights are specific weights.

Gram-atomic weights. Consider the gram-molecular weights of some pure substances containing hydrogen, and find the amount of this element contained in the gram-molecular weight in each case.

NAME OF SUBSTANCE CONTAINING HYDROGEN	GRAM-MOLECULAR WEIGHT	WEIGHTS OF THE ELEMENTS IN THE GRAM-MOLECULAR WEIGHT
Hydrogen chloride	36.5 gm.	hydrogen 1 gm.; chlorine 35.5 gm.
Hydrogen sulphide	34 gm.	hydrogen 2 gm.; sulphur 32 gm.
Methane	16 gm.	hydrogen 4 gm.; carbon 12 gm.
Phosphine	34 gm.	hydrogen 3 gm.; phosphorus 31 gm.
Acetylene	26 gm.	hydrogen 2 gm.; carbon 24 gm.
Hydrogen	2 gm.	hydrogen 2 gm.

In one gram-molecular weight of these substances, the number of grams of hydrogen is 1, 2, 3, or 4. If the gram-molecular weights of every hydrogen compound were listed, the *smallest* weight of hydrogen contained in these weights would be 1 gm.

The following table lists compounds containing carbon, their gram-molecular weights, and the weight of carbon in each gram-molecular weight.

NAME OF SUBSTANCE CONTAINING CARBON	GRAM-MOLECULAR WEIGHT	WEIGHT OF CARBON IN THE GRAM-MOLECULAR WEIGHT
Alcohol (ethyl)	46 gm.	24 gm.
Methane	16 gm.	12 gm.
Acetylene	26 gm.	24 gm.
Carbon dioxide	44 gm.	12 gm.
Carbon monoxide	28 gm.	12 gm.
Propane	44 gm.	36 gm.

The weights of carbon are 12, 24, or 36 gm. If the list were longer, the numbers 48, 60, etc., might occur under the *carbon* column, but the *smallest* weight would be 12 gm. and all other weights would be multiples of 12. The smallest weight of carbon contained in the gram-molecular weight of any of its compounds is 12 gm. Thus 12 gm. of carbon and 1 gm. of hydrogen could be called the **gram-atomic weights** of these elements.

To find the *gram-atomic weight* of oxygen:

1. List all the compounds that are gases (or that could be obtained as gases) containing oxygen as constituent.
2. Find the gram-molecular weight of each compound.
3. Find how much of this gram-molecular weight in each compound is oxygen.
4. Choose the smallest weight. This weight would be found to be 16 gm.

Atomic weight. It has previously been noted that:

1 gm. Hydrogen + 35.5 gm. Chlorine $\longrightarrow$ 36.5 gm. Hydrogen chloride and that 36.5 gm. is the gram-molecular weight of hydrogen chloride, and 36.5 is the molecular weight. If each molecule of hydrogen chloride weighs 36.5 units, then an atom of hydrogen weighs 1 unit and an atom of chlorine weighs 35.5 units.

If 36.5 represents the molecular weight of hydrogen chloride, then 1 and 35.5 must represent the relative weights of the atoms of hydrogen and chlorine. Thus the *numbers* 1, 35.5, and 16 are known as the **atomic weights** of hydrogen, chlorine, and oxygen, respectively and represent the relative weights of their atoms. In a similar manner the atomic weights of the other elements can be determined.

The atomic weights of the elements are always related to the atomic weight of *oxygen*, which is taken as 16.

There are other more accurate methods of determining atomic weights.

The kinetic-molecular theory. The existence of molecules and atoms helps the chemist to explain the behaviour of matter in chemical reactions. The physicist also relies on the molecule to explain many phenomena not involving a chemical change.

When a lump of sugar is put into water, the sugar apparently disappears. Actually the sugar is distributed through the water in such extremely small particles they cannot be seen even with the aid of a microscope. When water is exposed to dry air, it evaporates very rapidly. When a piece of iron is heated, it expands. When air is removed from a pair of Magdeburg hemispheres, there is difficulty in separating them. If a piece of chalk is cut in two, and the cutting process continued long enough, eventually pieces so small would be produced as to be no longer visible even under the most powerful microscope. Even after the practical limits of division of substances have been reached, this process could be pictured as going on and on. The remaining particle becomes smaller with each division. Could this supposed division go on forever? There is reason to believe that it could not.

Scientists believe that all material substances are composed of very small parts called molecules. A molecule of chalk cannot be divided and *still retain its identity as chalk*. Furthermore, there is reason to believe that the molecules are not jammed up against one another, but are separated by relatively large **inter-molecular spaces** and that molecules are always moving rapidly in this space. The difference in solid, liquid, and gaseous states is thought to be a difference in the energy of the molecules and hence to a difference in the inter-molecular spaces.

In the gaseous state, the inter-molecular spaces are very great; in liquids, the spaces are smaller; and in solids, the smallest of all. When there is a change in state (without a chemical change), a condition of temperature, or pressure, or both, has occurred and this results in a change in the size of the inter-molecular spaces. Thus, molecules of liquid water, ice, and steam are the same. The difference in state is a difference in the "spacing" of the molecules and in the energy content.

The phenomena mentioned at the beginning of this discussion can now be explained. The rapidly moving molecules of a solute would explain their **diffusion** through the inter-molecular spaces of the solvent. The movement of water molecules would explain the "escape" of some of them when water evaporates. Matter expands when heated because the heat makes the molecules move more rapidly and increases the size of the inter-molecular spaces. This increases the volume but not the mass. When air is removed from the Magdeburg hemispheres, the millions of molecules of air outside the hemispheres continue to "hammer" from all sides and, as there are few molecules left inside, the hemispheres are firmly *pushed* together.

Summary of the kinetic-molecular and atomic theories. 1. All matter (both elements and compounds) is made up of small particles called molecules and these are the smallest particles of matter that can have a separate existence. The weights of the different molecules are compared to the weight of the oxygen molecule which is 32.

2. Molecules are separated by inter-molecular spaces and are in a state of continuous motion.

3. Molecules in turn are made up of atoms. In an element, the atoms within each molecule are alike. Every compound contains at least two kinds of atoms.

4. An atom of an element cannot be divided into anything simpler (by ordinary chemical reaction).

5. The atoms of any one element are alike and have a definite weight. The weights of the different atoms are compared to that of the oxygen atom, whose weight is chosen as 16 units.

6. There are about 100 different kinds of atoms.

7. All chemical action takes place between atoms. An atom is the smallest part of an element that can take part in a chemical reaction, and all chemical action takes place by the inter-action of these atoms.

EXERCISE

A

1. (a) Define the equivalent weight of an element. (b) Distinguish between equivalent weight and gram-equivalent weight.

2. State the Law of Combining Weights.

3. State the Law of Multiple Proportions and illustrate your statement by reference to the two oxides of carbon.

4. Briefly compare the work of Dalton in developing the Laws of Definite and Multiple Proportions, with that of Gay-Lussac in his research with gases.

5. (a) State Gay-Lussac's Law of Volumes. (b) Enumerate four experiments performed by Gay-Lussac that led to the formulation of the law. (c) What was the experiment that initiated Gay-Lussac's research?

6. When 74 cc. of oxygen were added to 28 cc. of carbon monoxide and the mixture exploded, the product measured 88 cc. and consisted of 60 cc. of unused oxygen and 28 cc. of carbon dioxide. Show that this experiment illustrates Gay-Lussac's Law of Volumes.

7. (a) State the six assumptions made by Dalton in his chemical atomic hypothesis. (b) Why was Dalton's hypothesis soon elevated to the position of a theory?

8. (a) When the volumes occupied at S.T.P. by the gram-equivalent weights of all pure gases are determined by experiments, what amazing relationship occurs? (b) Show that Gay-Lussac's law of volumes could have been predicted from a knowledge of gram-equivalent weights and volumes.

9. (a) Why is 22.4 litres at S.T.P. selected as the gram-molecular volume? (b) What is the weight of 22.4 litres at S.T.P. of a pure gas called?

10. Describe how you could proceed to find the gram-molecular weight of water.

11. (a) State Avogadro's theory. (b) What new term was introduced by Avogadro to overcome misconceptions about Dalton's compound atom? (c) What is Avogadro's number?

12. (a) Distinguish clearly the difference between gram-molecular weight and molecular weight. (b) The molecular weight of carbon dioxide is 44. What is the gram-molecular weight of carbon dioxide?

13. (a) How would you proceed to find the gram-atomic weight of carbon? (b) Distinguish clearly between gram-atomic weight and atomic weight. (c) The atomic weight of nitrogen is 14. What does this mean?

14. Use the molecular theory to explain (a) the homogeneity resulting by continuously shaking sugar and water together; (b) the evaporation of water; (c) the pressure exerted by air or any other gas on the walls of a container; (d) that solids expand when heated.

15. (a) Distinguish between atoms and molecules. (b) Every molecule of sulphuric acid contains two atoms of hydrogen, one atom of sulphur, and four atoms of oxygen. Using a square to represent an atom of hydrogen, a triangle to represent an atom of sulphur, and a circle to represent an atom of oxygen, graphically represent a sulphuric acid molecule.

B

1. In an experiment it was found that 0.845 grams of magnesium combined with 0.563 grams of oxygen to form magnesium oxide. Calculate the gram-equivalent weight of magnesium.

2. Zinc oxide contains 80.3 per cent zinc. Find the equivalent weight of zinc.

3. When 8.00 grams of cupric oxide were reduced to copper by passing hydrogen over the hot oxide, 6.39 grams of copper were formed. Find the equivalent weight of copper.

4. Calculate the equivalent weights of the metals in their respective oxides, given the percentage of the metal in each case.

Calcium oxide	71.5 % calcium
Potassium oxide	83.0 % potassium
Ferrous oxide	77.73% iron
Aluminum oxide	52.95% aluminum

5. When 6.5 grams of zinc are added to hydrochloric acid, 0.2 grams of hydrogen are displaced. Find the equivalent weight of zinc.

6. Calculate the equivalent weight of the element from the following: (a) 14 gm. iron filings heated with excess sulphur form 22 gm. iron sulphide (E.W. sulphur = 16). (b) 2.00 gm. of a metal heated in chlorine yields 2.742 gm. of the chloride (E.W. chlorine = 35.5).

7. (a) Define combining weight. (b) If 100 grams of oxygen combine with 393.75 grams of copper, what is the combining weight of copper?

8. Carbon and oxygen combine to form two different oxides, carbon monoxide and carbon dioxide. Analysis shows that carbon monoxide contains 42.86% carbon and 57.14% oxygen, and that carbon dioxide contains 27.27% carbon and 72.73% oxygen. Show that these two oxides of carbon illustrate the Law of Multiple Proportions.

9. Nitrogen and oxygen combine to form three different oxides having the following percentage compositions:

	<i>Nitrogen</i>	<i>Oxygen</i>
Oxide A	63·6%	36·4%
Oxide B	46·7%	53·3%
Oxide C	30·4%	69·6%

Show that these three oxides of nitrogen illustrate the Law of Multiple Proportions.

10. Tin and oxygen form two oxides. One contains 78·77% tin, and the other 88·12% tin. Show that these oxides illustrate the Law of Multiple Proportions.

11. If 326 ml. of a gas at S.T.P. weigh 0·492 grams, find the gram-molecular weight. What is the molecular weight of this gas?

12. If 426 ml. of a gas measured at 27° C. and 640 mm. pressure weigh 0·492 gm., calculate the gram-molecular weight of the gas.

13. One litre of chlorine at S.T.P. weighs 3·18 gm. Find its molecular weight.

14. Calculate the gram-molecular weight of a gas, 642 ml. of which at 100° C. and 740 mm. pressure weigh 1·61 grams.

15. The gram-molecular weight of a gas is 80 gm. Calculate the volume occupied at S.T.P. by one gram of this gas.

16. The following list contains the gram-molecular weights and the percentage of chlorine in a few of its many compounds.

	<i>G.M.W.</i>	<i>per cent Chlorine</i>
Chlorine	71	100·
Chlorine monoxide	87·0	81·61
Hydrogen chloride	36·5	97·26
Carbon tetrachloride	154·0	92·20
Chloroform	119·5	89·1

From this very limited list, find the atomic weight of chlorine.

CHAPTER 12

Symbols, Formulae, and Equations

The secret of a good memory is attention, and attention to a subject depends upon our interest in it. We rarely forget that which has made a deep impression on our minds.

TRYON EDWARDS

The alchemists used symbols to represent substances. Because the success of their art depended on secrecy and superstition, they

 Fire	 Copper <i>Cuprum</i> Cu	 Gold <i>Aurum</i> Au	 Iron <i>Ferrum</i> Fe	 Lead <i>Plumbum</i> Pb
 Earth	 Mercury <i>Hydrargyrum</i> Hg	 Silver <i>Argentum</i> Ag	 Tin <i>Stannum</i> Sn	 Sulphur S
 Water				

Fig. 12.1. Some symbols used by the alchemist. The modern symbol for each element selected is also given.

purposely used signs and symbols to keep it enshrouded in mystery. Often the symbol selected had a definite reference to a property of a substance. The *ankh*, meaning everlasting, and consisting of a circle surmounting a cross, was the symbol for copper, because the Egyptians who used copper tools said, "No matter how much we use our axes, the metal never seems to wear out." Some of the symbols used were derived from the sun, the moon, or the stars; others from demons and

gods; and some apparently were meaningless. More than three thousand symbols have occurred in the history of alchemy. Dalton was the first chemist to use symbols to represent the atoms of the elements, but because they were inappropriate they were never widely used.

SYMBOLS

International symbols. To establish uniformity in the study of chemistry throughout the world, international chemical societies adopted a system advocated in 1813 by Johann Berzelius, a Swedish

15 th Century	16 th Century	17 th Century	1783 Bergman	1808 Dalton	1814 Berzelius	
					Au	Gold
					Hg	Mercury
					Pb	Lead

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Fig. 12.2. The evolution of a few symbols.

chemist. Berzelius used letters to represent the atoms of each element, and suggested the first letter of the name of the element as a suitable abbreviation. With nearly 100 elements and only 26 letters in the alphabet, a difficulty arose right away. To overcome this, a second small letter was used after the first capital letter as a symbol for some elements. Carbon, cobalt, calcium, chlorine, and copper all begin with "C". Obviously "C" cannot be used as a symbol for each of the preceding, so **C** is used for carbon, **Co** for cobalt, **Ca** for calcium, **Cl** for chlorine, and **Cu** (Latin, *cuprum*) for copper. The symbols for many other elements are also derived from their names in different languages. *A chemical symbol is a capital letter, or a capital letter followed by a small letter, and represents:*

1. One atom of the element.
2. The weight of one atom of the element compared with the weight of an oxygen atom.

Cl represents one atom of chlorine, one atomic weight of chlorine, or 35.5 parts by weight of chlorine. The relative weights of the elements in a compound are indicated by the symbols used to represent them.

The following symbols of some of the most important elements should be memorized:

SYMBOLS OF COMMON ELEMENTS

Aluminum	Al	Magnesium	Mg
Antimony (stibium)	Sb	Manganese	Mn
Arsenic	As	Mercury (hydrargyrum)	Hg
Barium	Ba	Nitrogen	N
Bromine	Br	Oxygen	O
Calcium	Ca	Phosphorus	P
Carbon	C	Potassium (kalium)	K
Chlorine	Cl	Silicon	Si
Copper	Cu	Silver (argentum)	Ag
Fluorine	F	Sodium (natrium)	Na
Hydrogen	H	Sulphur	S
Iodine	I	Tin (stannum)	Sn
Iron (ferrum)	Fe	Zinc	Zn
Lead (plumbum)	Pb		

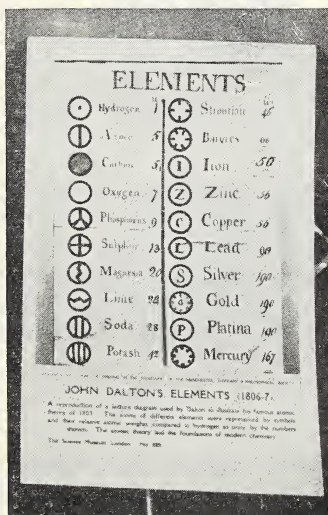
Because a symbol stands for a definite weight of an element, it is not correct to use a symbol merely as a short method of representing a name.

FORMULAE

A chemical **formula** is made up of symbols placed side by side. A symbol represents an atom of an element. A formula represents a molecule, and shows the elements of which the compound is composed and also the proportions in which they are united. When an atom of one element occurs more than once in a molecule, a small number below and to the right of the symbol in the formula indicates the number of atoms of that element. Thus H_2O shows that 2 atoms of hydrogen are joined with 1 atom of oxygen to form 1 molecule of water.

Both compounds and elements have formulae. There are two kinds of formulae, **simple** and **molecular**.

Simple formulae. A simple formula shows the simplest ratio in



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Fig. 12.3. A page from Dalton's notebook showing some of the symbols he used.

which the atoms combine, and is assigned to all substances of undetermined gram-molecular weights.

Molecular formulae. A molecular formula is given to a pure substance that can be weighed in the form of a gas. The formula not only shows the ratio in which the atoms combine, but also the weight of 22.4 litres of this gas at S.T.P. (i.e. the gram-molecular weight).



Fig. 12.4. Jacob Berzelius (1779-1848), a Swedish chemist, suggested the chemical symbols that scientists use to-day.

If the formula of a gas is known, a great deal of information is revealed. The molecular formula of carbon dioxide, CO_2 , indicates:

1. 44 units by weight of carbon dioxide.
2. That 22.4 litres of carbon dioxide at S.T.P. weigh 44 gm.
3. That every 44 gm. of carbon dioxide contain 12 gm. of carbon and 32 gm. of oxygen.
4. That when carbon dioxide enters into a chemical reaction, 44 gm. (or some simple multiple of it) react with the combining weight in grams (or some simple multiple of the combining weight) of some other pure substance.

Finding simplest formulae. In order to find the formula of any compound, either an analysis or a synthesis must be made. In Chapter 9 the results of an analysis of mercuric oxide were given, in which 1.320 gm. of mercury were combined with 0.105 gm. of oxygen to form 1.425 gm. of mercuric oxide.

Since 200 grams of mercury are represented by the symbol Hg ., the weight of oxygen that would unite with 200 grams of mercury would be

$$\frac{200}{1.320} \times 0.105 = \text{appr. } 16 \text{ gm. oxygen.}$$

But 16 gm. of oxygen can be represented by the symbol O . Therefore the simplest formula of mercuric oxide is HgO . Since mercuric oxide has never been obtained as a gas, HgO is the formula used to represent a combining weight of this compound.

Problem. An analysis of sodium oxide showed its composition to be 74.2% sodium and 25.8% oxygen. Find its formula. ($\text{Na} = 23$, $\text{O} = 16$)

Solution. 74.2 gm. sodium are united with 25.8 gm. oxygen.

$\therefore$ 23 gm. sodium will unite with $\frac{23}{74.2} \times 25.8 = \text{appr. } 8 \text{ gm. oxygen.}$

However, before O can be written for oxygen, there must be 16 gm. (or other units of weight). Multiplying by 2 shows that 46 gm. of sodium are united with 16 gm. of oxygen, and the simplest formula of the compound is Na_2O .

ALTERNATIVE SOLUTION

Weight of element	Ratio of atoms	Ratio in whole numbers	Formula
Sodium 74.2 gm.	$\frac{74.2}{23} = 3.226$	$\frac{3.226}{1.613} = 2$	Na_2O
Oxygen 25.8 gm.	$\frac{25.8}{16} = 1.613$	$\frac{1.613}{1.613} = 1$	

Finding the molecular formula of a gaseous element. The symbol O represents 1 gram-atomic weight, or 16 gm. of oxygen, but since oxygen is a gas, its formula must represent the weight of 22.4 litres at S.T.P. In an experiment, 186.7 cc. of oxygen, collected at S.T.P., were found to weigh 0.267 gm.

186.7 cc. oxygen at S.T.P. weigh 0.267 gm.

22,400 cc. oxygen at S.T.P. weigh $\frac{22400}{186.7} \times 0.267 = \text{appr. } 32 \text{ gm.}$

Since O represents 16 gm. of oxygen, 32 gm. would be represented by O_2 , the molecular formula of oxygen. By similar methods the formulae of hydrogen, nitrogen, and chlorine are found to be H_2 , N_2 , and Cl_2 , respectively. All active elements that exist as gases at ordinary temperatures have 2 atoms in each molecule, i.e. they are diatomic.

Finding the molecular formula of a compound. To find the molecular formula of a compound, it is necessary to know:

1. Its existence as a gas.
2. Its composition by weight.
3. Its density.

Problem. A certain gas was shown to have the composition of 50% sulphur and 50% oxygen. 1 litre of the gas at S.T.P. weighed 2.85 gm. Calculate (1) its simplest formula and (2) its molecular formula. ($\text{S} = 32$, $\text{O} = 16$)

Solution. Calculate the weight of oxygen combining with 1 gram-atomic weight of sulphur.

50 gm. sulphur combine with 50 gm. oxygen.

32 gm. sulphur combine with 32 gm. oxygen.

32 gm. of sulphur can be represented by the symbol S and 32 gm. of oxygen by O_2 . Therefore the simplest formula of the compound is SO_2 . Other formulae showing the same ratio of the atoms could be S_2O_4 ; S_3O_6 ; S_4O_8 ; etc.

But the formula of a gas must represent the weight of 22.4 litres at S.T.P. At S.T.P., 22.4 litres of this gas weigh $22.4 \times 2.85 =$ appr. 64 gm. The molecular formula must be SO_2 since this formula represents 64 gm.

Problem. A gaseous compound of carbon and hydrogen contains 92.3% carbon and 7.7% hydrogen. At S.T.P., 1 litre of the gas weighs 1.161 gm. Find its true, or molecular, formula. (C = 12, H = 1)

Solution.

92.3 gm. carbon are united with 7.7 gm. hydrogen.

12 gm. carbon are united with $\frac{12}{92.3} \times 7.7 =$ appr. 1 gm. hydrogen.

$\therefore$ 1 atom of carbon is united with 1 atom of hydrogen.

Thus the simplest formula would be CH. Other possible formulae could be C_2H_2 ; C_3H_3 ; C_4H_4 ; etc.

But the molecular formula of a gas represents the weight of 22.4 litres at S.T.P. At S.T.P. 22.4 litres of this gas weigh $22.4 \times 1.161 =$ appr. 26 gm. Therefore the formula selected must represent 26 gm., and this formula is C_2H_2 .

Alternative solution. Since the compound is gaseous, the formula must represent the weight of 22.4 litres at S.T.P., which is 26 gm. It is known that 100 gm. of the gas contain 92.3 gm. carbon and 7.7 gm. hydrogen. Therefore, 26 gm. of the gas contain 24 gm. carbon and 2 gm. hydrogen. Therefore the molecular formula is C_2H_2 .

Percentage composition from a formula. Since the proportion by weight of the constituents must be known before a formula can be given to a compound, it follows that when the formula is known to the chemist, he can calculate the percentage composition of the compound.

Problem. $KClO_3$ is the formula for potassium chlorate. Find the percentage composition. (K = 39, Cl = 35.5, O = 16)

Solution. $KClO_3$ could represent $39 + 35.5 + 48 = 122.5$ gm.

122.5 gm. potassium chlorate contain 39 gm. potassium, 35.5 gm. chlorine, and 48 gm. oxygen.

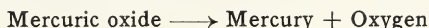
100 gm. potassium chlorate contain $\frac{39}{122.5} \times 100 = 31.8$ gm. potas-

sium, $\frac{35.5}{122.5} \times 100 = 29$ gm. chlorine, and $\frac{48}{122.5} \times 100 = 39.2$ gm. oxygen.

Potassium chlorate is therefore 31.8% potassium, 29% chlorine, and 39.2% oxygen by weight.

CHEMICAL EQUATIONS

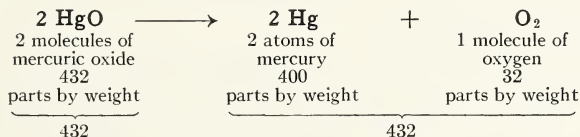
Up to this point chemical reactions have been represented by "word equations", for example:



Experiments have shown that 216 gm. of mercuric oxide, when heated, give off 200 gm. of mercury and 16 gm. of oxygen. This information can be expressed as follows:



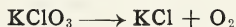
In all chemical equations, molecular formulae are required for gaseous pure substances, hence the molecular formula for oxygen, O_2 , must be used. Two molecules of mercuric oxide are required to produce one molecule of oxygen. Hence the equation is correctly written as follows:



If a chemical equation is to be of value, every detail must be correct. Before an equation can be written, the following information is necessary:

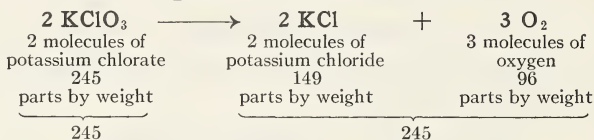
1. The names of the reacting substance or substances, and the names of the substance or substances formed by the reaction.
2. The formulae of all the substances involved.

When these facts are known, a "skeleton" equation can be written. The same number of atoms must be represented on each side of a "balanced equation," in order to conform to the Law of Conservation of Mass. The **balancing** of the equation represents a simple problem in arithmetic. Thus, if it is known that when potassium chlorate is heated, potassium chloride and oxygen are formed, and that the formula of potassium chlorate is KClO_3 , of potassium chloride KCl , and of oxygen O_2 , then the "skeleton" can be written as follows:



This shows that 122.5 units by weight of potassium chlorate decom-

pose to form 74.5 units by weight of potassium chloride, and 32 units by weight of oxygen. But since a change in *total* weight never occurs in a chemical reaction it is necessary to balance the weights as follows:

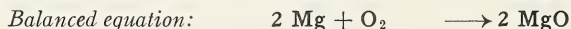
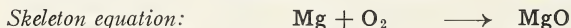
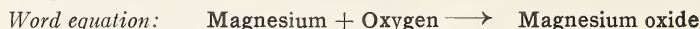


A balanced equation is a concise statement of a chemical change, using formulae instead of words. An equation cannot be predicted. It can only be written if the substances entering into the reaction and the products formed are known. The formulae used in a "skeleton" equation are found by experiment, express facts, and cannot be altered. If the "skeleton" equation requires *balancing*, the numbers of molecules taking part in the reaction are adjusted.

Rules for writing chemical equations.

1. From a knowledge of the facts, write the word equation.
2. Substitute formulae for words.
3. Balance the equation.

Consider the chemical reaction resulting when magnesium is burned in oxygen.



Only the balanced equation can properly be referred to as a chemical equation.

EXERCISE

A

1. Why did the early chemical symbols prior to Berzelius display no uniformity? Why were they of little value?

2. (a) What is a chemical symbol? (b) What three facts does a chemical symbol represent? (c) Illustrate your answer in (b) by reference to the symbol **H**, and the symbol, **O**.

3. (a) How were the modern chemical symbols of Berzelius derived? (b) List the elements whose symbols have been derived from their Latin names and give the Latin name and symbol in each case. (c) Why was it necessary to go back to the Latin names to derive the symbols for these elements? (d) Are symbols, formulae and equations different in other languages such as Russian or German?

4. The symbols for some of the commoner elements have been listed in a table in this chapter and should be memorized. The symbols and atomic weights

of less common elements will be found in a table in the appendix. What are the chemical symbols for gold, platinum, argon, neon, fluorine, nickel?

5. (a) What is a chemical formula and what does it represent? (b) To what substances is a simplest, or empirical, formula given, and what information does it reveal? (c) What is a true, or molecular formula and how does it differ from the "simplest" formula?

6. In assigning a true formula to a particular compound, an analysis or a synthesis must be made in order to determine three facts. Name these three facts.

7. What information is conveyed by the true, or molecular, formula for (a) carbon dioxide gas (CO_2); (b) acetylene gas (C_2H_2); (c) nitrogen gas (N_2)?

8. What does each of the following represent: Ra, U, H, H_2 , 2 H_2 , 2 H, O, O_2 , 3 O_2 , 3 O, 2 O_3 ?

B

In solving all problems involving atomic weights, use the approximate atomic weights given on inside back cover.

I. Problems involving the determination of formulae

1. An oxide of nitrogen, upon analysis, was found to have the following percentage composition: nitrogen 46.7%, oxygen 53.3%. Calculate the simplest formula of this compound.

2. An oxide of iron on analysis was found to contain 70% iron and 30% oxygen. Determine its simplest formula.

3. Calculate the simplest formula of a compound containing 90.66% lead, and 9.34% oxygen.

4. An oxide of mercury weighing 78 gm. was decomposed by heating and 3.0 gm. of oxygen were evolved. Find the simplest formula of this oxide.

5. When 2.61 gm. aluminum were burned in oxygen, the product weighed 4.921 gm. Determine the simplest formula of aluminum oxide.

6. Phosphorus forms two oxides containing 43.6% and 56.5% of phosphorus respectively. Calculate the simplest formulae of these two oxides of phosphorus.

7. Upon analysis, a compound was found to have the following composition by weight: carbon 40%, oxygen 53.33%, and hydrogen 6.67%. Find the simplest formula of the compound.

8. (a) A compound contains 64.86% carbon, 13.51% hydrogen, and 21.62% oxygen. What is the simplest formula of this compound? (b) What further data would you require to determine the true (molecular) formula of this compound?

9. From the analytical results given, find the simplest formulae of the following compounds: (a) sodium 39.31%, chlorine 60.68%; (b) iron 8.4 gm., sulphur 9.6 gm.; (c) calcium 29.41%, sulphur 23.52%, oxygen 47.05%; (d) silver 70.13%, nitrogen 9.09%, oxygen 20.77%; (e) sodium 27.38%, hydrogen 1.19%, carbon 14.29%, oxygen 57.14%; (f) sodium 19.17%, hydrogen 0.83%, sulphur 26.66%, oxygen 53.33%.

10. A compound was found to have the simplest formula CH_2O . The molecular weight was found to be approximately 179.8 gm. What is the true formula of this compound?

11. A gaseous compound having a molecular weight of 30 is composed of carbon 39.95%, hydrogen 6.69%, and oxygen 53.36%. Calculate the true formula of this compound.

12. Upon analysis, a gaseous compound was found to contain 75% carbon and 25% hydrogen. 22.4 litres of this gas at standard conditions weighed 16 gm. What is the true formula of the gas?

13. A gaseous compound of carbon and hydrogen contains 80% carbon. One litre of this gas at S.T.P. weighs 1.34 gm. Find the molecular formula of this gas.

14. A certain compound was vaporized and 250 cc. of the vapour, considered at standard conditions, weighed 1.55 gm. Its composition was found to be 22.6% phosphorus, and 77.4% chlorine. What is the true formula of this compound?

15. A certain gaseous compound weighs 0.251 gm. per 200 cc. (S.T.P.) and is composed of 85.71% carbon and 14.28% hydrogen. Find the molecular formula of this gas.

16. A compound contains 85.71% carbon and 14.28% hydrogen. One litre of this gas at 25° C. and 746 mm. pressure weighs 1.141 gm. Find the true formula of this compound.

17. What is the molecular formula of a gas that is composed of 82.35% nitrogen and 17.65% hydrogen, and is 8.5 times as dense as hydrogen gas?

18. A compound contains 24.24% carbon, 4.04% hydrogen, and 71.72% chlorine. Its vapour density referred to hydrogen ($H = 1$) is 49.5. Find its true formula.

19. Calculate a possible formula for a hydrate having the following percentage composition: sodium 16.08%, carbon 4.19%, oxygen 16.76%, and water 62.96%.

20. Ten grams of a certain salt contain 1.71 gm. sodium, 1.19 gm. sulphur, 4.7 gm. water, the rest being oxygen. Calculate a possible formula for the salt.

II. Problems involving formula weights and percentage composition

1. Calculate the "formula weights" of the following compounds from the information given in their formulae: (a) potassium chloride— KCl ; (b) calcium hydroxide— $Ca(OH)_2$; (c) aluminum sulphate— $Al_2(SO_4)_3$; (d) ethyl alcohol— C_2H_5OH ; (e) ammonium carbonate— $(NH_4)_2CO_3$; (f) bluestone— $CuSO_4 \cdot 5 H_2O$; (g) washing soda— $Na_2CO_3 \cdot 10 H_2O$; (h) acetic acid— CH_3COOH ; (i) calcium phosphate— $Ca_3(PO_4)_2$; (j) plaster of Paris— $(CaSO_4)_2 \cdot H_2O$.

2. Find the percentage composition of (a) potassium chlorate— $KClO_3$; (b) ferric oxide— Fe_2O_3 ; (c) ammonium sulphate— $(NH_4)_2SO_4$.

3. Find the percentage composition of Epsom salts, $MgSO_4 \cdot 7 H_2O$.

4. Calculate the percentage composition of the following compounds: (a) sucrose— $C_{12}H_{22}O_{11}$; (b) phosphorus pentoxide— P_2O_5 ; (c) tartaric acid— $H_2C_4H_4O_6$; (d) potash alum— $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$.

5. (a) What is the percentage of calcium in calcium phosphate, $Ca_3(PO_4)_2$? (b) What weight of phosphorus (P) could be obtained from 2000 pounds of calcium phosphate?

6. Calculate (a) the percentage composition of bluestone— $CuSO_4 \cdot 5 H_2O$; (b) the percentage of water in bluestone; (c) the percentage of anhydrous copper sulphate in bluestone.

7. An ore of aluminum called bauxite has the formula $Al_2O_3 \cdot 2 H_2O$. What weight of bauxite would be needed for the extraction of one ton of aluminum?

8. Find the weight of iron in one ton of an ore containing 75% ferric oxide (Fe_2O_3).

9. When 0.726 gm. magnesium were burned in oxygen, 1.210 gm. magnesium oxide were formed. Calculate the percentage composition of magnesium oxide.

10. When 3.468 gm. hydrated sodium sulphate were heated, 2.122 gm. anhydrous sodium sulphate were formed. What percentage of water of hydration does hydrated sodium sulphate contain?

III. Problems involving molecular formulae

1. From the formula for ammonia gas, NH_3 , calculate (a) the gram-molecular weight of this gas; (b) the molecular weight; (c) the weight of 10 litres at standard conditions; (d) the weight of 100 cc. at S.T.P.; (e) the volume occupied by 2 grams of ammonia under standard conditions; (f) the weight of 500 cc. of this gas, the volume being measured at 20°C . and 730 mm. pressure; (g) the density of ammonia compared with hydrogen; (h) the density of ammonia compared with air.

2. If 500 cc. of carbon dioxide gas (CO_2) at standard conditions weigh 0.984 gm., calculate the gram-molecular weight, the molecular weight, the volume occupied by one gram of this gas at standard conditions, the weight of one litre measured at 35°C . and 640 mm. pressure, and the density of this gas compared with hydrogen.

3. Calculate from the formula given in each case the weight of one litre of each of the following gases, or vapours, considered at S.T.P.: nitrous oxide, N_2O ; methane, CH_4 ; ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$; hexane, C_6H_{14} ; glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$.

4. What volume at S.T.P. will be occupied by (a) 4 gm. oxygen (O_2), (b) 25 gm. chlorine (Cl_2), (c) 16 gm. sulphur dioxide (SO_2), (d) 12.5 gm. nitrogen dioxide (NO_2)?

5. A compound has the molecular formula CHCl_3 . What volume of its vapour at 100°C . and 2 atmospheres (1520 mm.) pressure must be taken to have a weight of 50 gm.?

6. (a) Calculate the molecular weight of a gas, knowing that 5 cc. of this gas at S.T.P. weigh 0.01430 gm. (b) What is the molecular weight of a gas when 652 ml. at standard conditions weigh 0.984 gm.? (c) Calculate the molecular weight of a gas when 652 ml. measured at 25°C . and 759 mm. pressure weigh 0.984 gm. (d) What is the weight of 3 litres of hydrogen chloride gas (HCl) at 21°C . and 72.4 cm. pressure?

7. Under standard conditions, one litre of oxygen weighs 1.43 gm. and one litre of hydrogen weighs 0.09 gm. What is the approximate relation between the weight of a molecule of oxygen and that of a molecule of hydrogen? Why?

8. (a) The density of a gas compared to hydrogen is 39. Calculate the molecular weight of this gas. (b) The density of a gas compared to oxygen is 2.45. Find its molecular weight. (c) The density of a gas compared to air is 2.45. Find its molecular weight.

9. Calculate the molecular weight of oxygen from the following data:

Weight of test-tube + potassium chlorate before heating	11.904 gm.
Weight of tube and residue after heating	11.395 gm.
Volume of oxygen evolved	400.50 cc.
Temperature of the evolved gas	17°C .
Barometric pressure	720 mm.

10. Assuming air to be a mixture by volume of 80% nitrogen (N_2) and 20% oxygen (O_2), calculate the weight of one litre of air at S.T.P.

11. When measured in a dry condition at S.T.P., 0.8 grams of a certain gaseous element were found to occupy 640 cc. If this element has a diatomic molecule, what is the atomic weight of the element?

C

1. What facts can a chemist learn from a *formula equation* that are not revealed by a *word equation*?

2. What three facts must the student possess before he can write a correct skeleton equation?

3. What relations do the Law of Conservation of Mass and the Law of Definite Proportions bear to a balanced chemical equation?

4. Outline the steps suggested in the text for writing a correct balanced equation.

5. Using the steps suggested in Question 4, write balanced chemical equations for the following reactions: (a) A mixture of hydrogen (H_2) and oxygen (O_2) gases form water (H_2O) when exploded in a eudiometer tube. (b) A solution of sodium hydroxide ($NaOH$) reacts with sulphuric acid (H_2SO_4) to produce sodium sulphate (Na_2SO_4) and water (H_2O). (c) Calcium carbonate ($CaCO_3$) reacts with hydrochloric acid (HCl) to form calcium chloride ($CaCl_2$), water (H_2O), and carbon dioxide (CO_2). (d) Sodium nitrate ($NaNO_3$) decomposes when heated and yields sodium nitrite ($NaNO_2$) and oxygen (O_2). (e) Aluminum metal (Al) reacts with hydrochloric acid (HCl) to form aluminum chloride ($AlCl_3$) and hydrogen (H_2).

CHAPTER 13

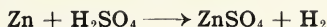
Valence

Again, things which look to us hard and dense must consist of particles hooked together, and to be held in union because compacted throughout with branch-like elements.

LUCRETIVS

The substitution of chemical symbols and formulae in the word equations with which we are already familiar presents certain complications. What formulae, for example, will be used to represent the various compounds? Memorization of the formulae of the countless possible compounds would be very difficult if it were not for a knowledge of **valence** (sometimes called **valency**) of the elements they contain.

The meaning of valence. The equation for the preparation of hydrogen from zinc and dilute sulphuric acid is:



Here one atom of zinc displaces two atoms of hydrogen from a sulphuric acid molecule. Zinc is said to have a valence of two or to be **divalent**.

The following table gives the formulae of a few compounds containing hydrogen as a constituent, the formulae having been obtained from experimental data.

HCl
HBr

H₂O
H₂S

NH₃
PH₃

CH₄

The above formulae indicate that different elements combine differently with hydrogen. One atom of chlorine unites with one atom of hydrogen to form a molecule of hydrogen chloride. Chlorine is said to have a valence of one, or to be **univalent**. One atom of oxygen, however, unites with two atoms of hydrogen to form a molecule of water. Oxygen, therefore, is said to be **divalent**. Similarly nitrogen is **trivalent**, and carbon **quadrivalent**.

The valence of any element represents the number of atoms of hydrogen that will unite with, or be displaced by, one atom of that element. When an element does not combine with, or displace, hydrogen, its valence

can be determined by a study of its combination with some other element of known valence. Thus, although silver does not unite with hydrogen, it is considered univalent because one atom of silver combines with one atom of chlorine to form a molecule of silver chloride (AgCl), and the valence of chlorine (as shown in HCl) is one.

Elements with several valences. Some elements unite with others in more than one proportion. There are two chlorides of mercury; mercurous chloride has the formula HgCl , and mercuric chloride has the formula HgCl_2 . Since chlorine has a valence of one, mercury in the first compound has a valence of one, and in the second compound it has a valence of two.

Table of valences. The following table gives the commoner valences of the elements for which the symbols have already been given.

VALENCES OF VARIOUS ELEMENTS

<i>One</i>	<i>Two</i>	<i>Three</i>	<i>Four</i>	<i>Five</i>	<i>Six</i>
H	Ba	Al	C		
Na	Ca		Si		
K	Mg				
Ag	Zn				
Hg(ous)	Hg(ic)	As(ous)		As(ic)	
Cu(ous)	Cu(ic)	Sb(ous)		Sb(ic)	
	Pb				
	Mn		Mn(in MnO_2)		
	Fe(ous)	Fe(ic)			
	Sn(ous)		Sn(ic)		
F	O	N			
Cl	S (Sulphides)		S (in SO_2)		S (in SO_3)
Br		P(ous)		P(ic)	
I					

Using valence. If the valence of an element is known, the information can be used to write not only the formula of the compound formed when the element unites with hydrogen, but also the formulae of the compounds formed when it unites with other elements. The valence of aluminum is 3 because 1 atom of aluminum will combine with 3 atoms of chlorine to form a molecule of aluminum chloride. The aluminum atom can be pictured as having three "arms", or "couplers", each of which can couple with the one "arm" of a chlorine atom (Fig. 13.1 [1]).

The oxygen atom has a valence of 2. It can be pictured with 2 "arms", each grasping the "arm" of a hydrogen atom (Fig. 13.1 [2]). Fig. 13.2 [1] shows that 2 aluminum atoms are equivalent to 6 atoms of chlorine, and Fig. 13.2 [2] that 3 atoms of oxygen would be needed to

"look after" 6 atoms of hydrogen. Therefore, when aluminum and oxygen unite, they combine in the proportion of 2 atoms of aluminum

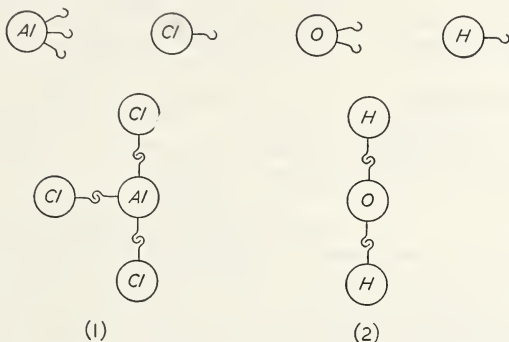


Fig. 13.1. Valence. 1, each atom of aluminum is represented as having three "arms", each "arm" grasping the single "arm" of a chlorine atom. 2, each oxygen atom has two "arms" and each hydrogen atom has one. Hence a single oxygen atom can hold in combination two atoms of hydrogen.

to 3 atoms of oxygen, and the formula of the oxide consequently is Al_2O_3 (Fig. 13.2[3]). By analysis, this is found to be the correct formula of aluminum oxide.

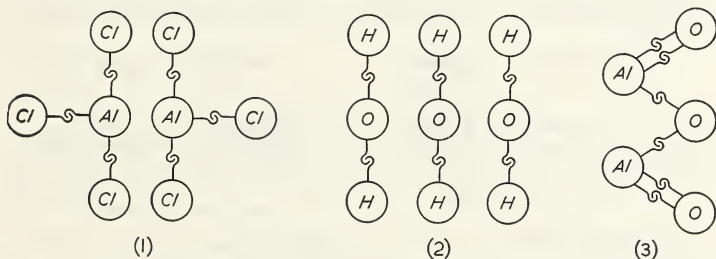


Fig. 13.2. Two atoms of aluminum, 1, can hold six atoms of chlorine; three atoms of oxygen, 2, can hold six atoms of hydrogen. Hence, 3, two atoms of aluminum will combine with three atoms of oxygen.

It will be noticed that *the numbers of atoms of the elements are in inverse proportion to their valences*. If this is kept in mind, the formulae of many compounds may be written. If the formula for aluminum carbide is to be written:

1. Write the symbols of the two elements concerned, and mark their valences above them. (It is customary to write the symbol for the metallic element first.)

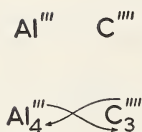


Fig. 13.3. The inverse rule of valence. The valence of each element is represented by the number of vertical lines above and to the right of each symbol.

2. "Criss-cross" with the valences, using small whole numbers below and to the right of the symbols (i.e. balance the valences using the inverse rule).

3. The formula is Al_4C_3 .

It is important to remember that *valence* is merely a device to aid the memory. Formulae can only be established by actual analyses.

In an elementary study of chemistry, it is customary to accept the above concept of valence as established in 1852. Basing valence upon hydrogen is quite an excellent procedure, since the hydrogen atom never combines with more than one atom of any other element. Thus, if the valence of hydrogen is taken as one, the valence of each of the other elements will of necessity always be a whole number. (There are no half atoms.)

Since 1911, however, scientists have been able to investigate the composition of matter to such an extent that we are now in a much better position to understand the manner in which many fundamental reactions and processes take place. This is especially true of valence.

One of the results of scientific research is a clearer concept of the structure of the atom. It is now believed that every atom is composed

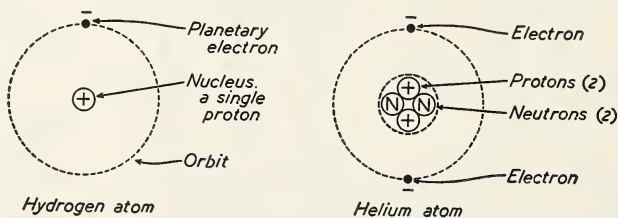


Fig. 13.4. The structure of the two simplest atoms.

of units of positive electricity called **protons**, and units of negative electricity called **electrons**. These protons and electrons are believed to be arranged in a very definite way with the protons contained in a central core, or **nucleus**, and the electrons in some characteristic arrangement outside the nucleus. The electrons are believed to revolve about the nucleus in a well-organized pattern of definite paths, or **orbits**, and since there is a similarity between their motion and the motion of the planets around the sun, they are sometimes referred to as **planetary electrons**.

Many attempts have been made to represent atomic structures graphically, but no representation is entirely satisfactory. There is still some doubt as to the exact nature of the arrangement; moreover, it is difficult to represent a three dimensional structure on the plane surface of a book.

It is customary to use diagrams similar to the following to represent atomic structure.

These diagrams are designed to illustrate that:

1. The electrons are arranged in **rings, shells**, or orbits about the nucleus of protons and neutrons.
2. The hydrogen and sodium atoms are alike in that they each have one electron in the outer ring.
3. The chlorine atom has an inner ring of two electrons, a second ring of eight electrons, and an outer ring of seven electrons.
4. The argon atom has two electrons in the inner ring, and eight in each of the next two rings.

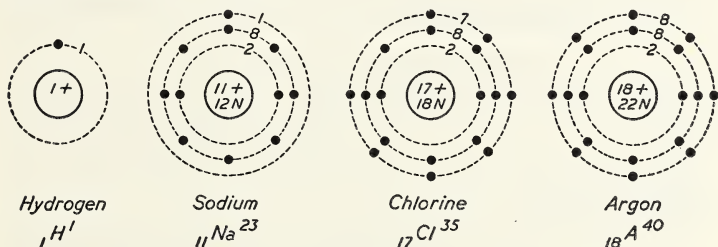


Fig. 13.5. The hydrogen atom has a valence of + 1, the sodium atom of + 1, the chlorine atom of - 1, and the argon atom of zero. Compare the valences with the number of electrons in the outer shell of each atom. The atomic number is represented below and to the left of each symbol, and the atomic weight above and to the right.

There are neutrons present in the nucleus along with the protons. As the neutrons are electrically neutral and add only to the mass of the atom, they will not be discussed further in this elementary treatment.

The arrangement of electrons is not completely understood. Research has shown, however, that the electrons probably revolve about the positively charged nucleus and at definite distances from it. Each electron is considered to have its own independent path or orbit. Most chemists are convinced that all chemical activity is related directly to electrons, and that the electron theory explains the chemical properties of the elements. This explanation is based on one or two important facts.

There are six gases (helium, neon, argon, krypton, xenon, and radon), known as the inert gases, and these never enter into any chemical combinations. This lack of chemical activity is explained on the assumption that the electrons of these inert elements are so arranged with eight electrons in the outer shell (except helium which is complete with two) as to give their atoms **perfect stability** (Fig. 13.6).

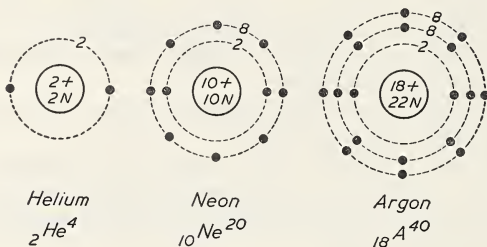


Fig. 13.6. The stable atoms of helium, neon, and argon. These elements do not combine with other elements.

In contrast, it is assumed that the chemical activity of all the other elements is caused by the tendency of each to gain or lose electrons in order to acquire this same perfect stability of eight electrons in the outer shell.

Fig. 13.8 shows an electron configuration for each of the first eighteen elements.

The following table gives the number of electrons in the successive shells of the six inert gases. In addition to showing the maximum number of electrons possible in each shell, the table shows that there are never more than eight electrons in the outermost shell. For this reason it is usually referred to as "the stable **octet** structure" of an atom.

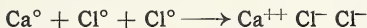
<i>Element</i>	<i>Atomic weight</i>	<i>Atomic number</i>	<i>Shells</i>					
			i	ii	iii	iv	v	vi
Helium	4.003	2	2					
Neon	20.183	10	2	8				
Argon	39.944	18	2	8	8			
Krypton	83.7	36	2	8	18	8		
Xenon	131.3	54	2	8	18	18	8	
Radon	222.0	86	2	8	18	32	18	8

Electrons may shift from one atom to another, and elements tend either to **lend** or **borrow** electrons in order to make the outer ring a complete shell with the required number of eight electrons. It is obvious that the sodium atom could very easily lend its single electron

in the outer ring, and return to the smaller, stable, complete ring structure of eight electrons. Likewise the chlorine atom could very easily borrow a single electron to complete its outer ring. Actually this is what happens during a chemical reaction between sodium and chlorine. Each sodium atom loses an electron, and at the same time each chlorine atom gains this electron. If the sodium atom is represented by the symbol Na° , then the sodium atom with its excess positive charge could be represented by Na^+ , and as such is known as the sodium **ion** (Chapter 16). Likewise the chlorine atom, Cl° , becomes Cl^- and assumes the role of a chloride ion.

The hydrogen atom, H° , can also lend its single electron to become the hydrogen ion H^+ . Since the hydrogen atom has only one electron to lend we can see why it never combines with more than one atom of any other element, and why its choice as a standard of valence in 1852 was a good one.

When a bivalent metal, like calcium, gives up electrons to a univalent non-metal like chlorine, the metallic atom can furnish enough electrons to complete the outer rings of *two* chlorine atoms:



These ideas of positive and negative ions can now be related to accepted explanations of valence.

1. Valence is the word used to express the charge acquired by an atom when it lends or borrows electrons during a chemical reaction.

2. When an element lends electrons, it becomes electro-positive. All electro-positive elements act as metals.

3. When an element borrows electrons, it becomes electro-negative. All electro-negative elements act as non-metals.

In solid sodium chloride, the sodium atom that has lent its one electron to the chlorine atom is represented by Na^+ , while the

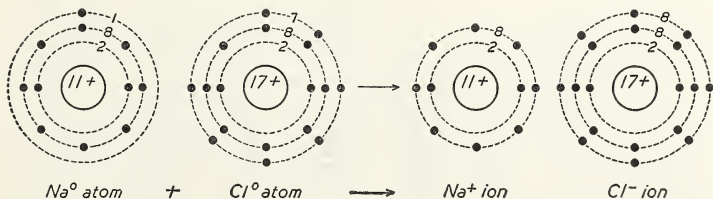
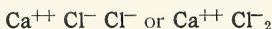


Fig. 13.7 The formation of solid sodium chloride. When an atom of sodium and an atom of chlorine combine to form solid sodium chloride the sodium atom "loans" an electron and thus assumes a stable form with eight electrons in the outer shell. The chlorine atom "borrows" this electron to complete its outer shell.

Groups							
	I	II	III	IV	V	VI	VII
Valences	+1	+2	+3	+4	+5	+6	+7
Periods	Note: 1. The Atomic Number is placed in the upper left corner. 2. The Atomic Weight is placed in the upper right corner.						
	1. 1.008  Hydrogen						2. 4.003  Helium
	3. 6.94  Lithium	4. 9.02  Beryllium	5. 10.82  Boron	6. 12.01  Carbon	7. 14.008  Nitrogen	8. 16.000  Oxygen	9. 19.00  Fluorine
2	11. 22.997  Sodium	12. 24.32  Magnesium	13. 26.97  Aluminum	14. 28.06  Silicon	15. 30.98  Phosphorus	16. 32.06  Sulphur	17. 35.457  Chlorine
	18. 39.944  Argon						

Fig. 13.8. The first eighteen elements, arranged in order of their atomic numbers. Atomic weights are shown in the upper right corner of each panel.

chlorine atom that has gained this electron is represented as Cl^- . Hence solid sodium chloride could be represented by $\text{Na}^+ \text{Cl}^-$ (Fig. 13.7) Calcium, however, being divalent, has two electrons to "give up", and so will require two chlorine atoms to "take" the electrons. The formula of calcium chloride could be written:



It is evident that the inverse rule of valence is the same as that given above. But with **electrovalence** the element giving up the electrons is shown as having a **positive** valence rather than just having a valence. The element that receives the electron is shown as having a negative valence.

Variable valences are also quite easily explained when atomic structures are studied in more detail. At present, it is suggested that the electrovalences be accepted and learned without question. However, when discrepancies seem to appear in the further study of chemistry, remember that the *usual* conduct of atoms has been referred to, and that atoms, like people, do not always behave in exactly the manner anticipated.

The more common electrovalences of a few elements are given below:

Valence

+1	H, Na, K, Ag, Hg(ous) Cu(ous)
-1	F, Cl, Br, I
+2	Ba, Ca, Mg, Zn, Hg(ic), Cu(ic), Pb, Mn(ous), Fe(ous), Sn(ous)
-2	O, S(in H_2S)
+3	Al, N, P(ous), As(ous), Sb(ous), Fe(ic)
-3	P, N
+4	C(in CO_2), Si, Mn (in MnO_2), Sn(ic), S(in SO_2), Pb (in PbO_2)
-4	C (in Al_4C_3)
+5	N, P(ic), As(ic), Sb(ic)
+6	S(in SO_3)

EXERCISE

A

1. (a) What is valence? What was chosen as the standard for valence?
(b) Explain in terms of hydrogen displacement, "the valence of a metal is three."
(c) Explain: (i) univalent; (ii) divalent; (iii) trivalent; (iv) quadrivalent.
2. From each of the following formulae find the valence of the metal constituent: ZnO , Na_2O , PbS , HgO , Hg_2O , CuCl_2 , FeO , Fe_2O_3 , AgCl .
3. What is meant by variable valence? Illustrate your answer by reference to the mercury and iron compounds whose formulae appear in the question above.
4. Using valence, write the formula for each of the following: potassium oxide, sodium chloride, cuprous oxide, cupric oxide, calcium sulphide and zinc chloride.
5. Describe the procedure necessary to establish the formula of a newly discovered compound which is (a) a salt that cannot be vaporized; (b) a gas at S.T.P.; (c) a liquid that can be vaporized at 78°C .

6. Cobalt (Co) is sometimes divalent and sometimes trivalent. What would probably be the formulae of its two oxides?

7. Chromium forms two oxides, chromous and chromic. Its symbol is Cr and its valences are two and three. Write the formulae of its oxides.

8. The element osmium (Os) sometimes shows octovalence. What is the simplest formula of the oxide of osmium (not a gas) where osmium exhibits this valence?

9. Platinum (Pt) forms bivalent and quadrivalent compounds. In platinum compounds the valence is 2. What is the formula for platinum chloride? What is the formula for platinum chloride?

B

1. (a) Why was the choice of the element hydrogen a good one upon which to base valence? (b) How does a knowledge of the structure of the sodium atom make it easier to understand the fact that sodium is univalent?

2. Using a diagram to represent an atom of chlorine, explain the following statements: (a) Chlorine is a non-metal. (b) Chlorine is univalent. (c) Chlorine may have a valence of -1 or $+7$. (d) Atoms tend to attain symmetry in preference to electrical neutrality. (e) Atoms tend to form a stable octet structure. (f) The nucleus of an atom contains neutrons. (g) An atom is electrically neutral. (h) Valence electrons are on the outside shell. (i) The number of protons determines the atomic number of an element.

3. In terms of atomic structure explain the following statements: (a) Helium is an inactive (inert) gas. (b) Sodium is an active metal. (c) Chlorine is an active non-metal. (d) Potassium is a more active metal than sodium. (e) Chlorine is a more active non-metal than iodine. (f) Fluorine is the most active non-metal. (g) Sodium chloride is a stable compound. (h) Magnesium is less active than potassium. (i) Nitrogen may have a valence of -3 or $+5$.

4. Write formulae (using electrovalence) for the following compounds: sodium bromide; sodium oxide; magnesium iodide; mercurous chloride; mercuric oxide; barium sulphide; aluminum oxide.

5. "All chemical activity is related directly to electrons." Explain this statement.

CHAPTER 14

Naming Compounds

Language is the only instrument of science, and words are but the signs of ideas.

SAMUEL JOHNSON

Every branch of science has a pertinent system of nomenclature involving a definite vocabulary which any student must master in order to understand the subject. Biology's system of naming and classification greatly simplifies the study of plants and animals. Plants are divided into phyla, classes, orders, families, genera, and species, and a common language is necessary in naming them. Thus the name *Quercus* immediately calls to mind the genus of plants commonly known as "the oaks". The addition of the word *alba* suggests the white oak, one of the species of the genus *Quercus*. *Quercus alba* is the name of the white oak.

Nomenclature in chemistry. Before Lavoisier's time, there was nothing systematic about the way compounds were named. Astrology and alchemy went hand in hand so closely that the influence of the astrologer is evident in the names of some compounds such as lunar caustic, and crocus martis. Mercuric oxide, made by one process, was called "mercurius calcinatus per se", and when produced by another method it was called "red precipitate". Such a system must have resulted in confusion, to say nothing of the strain on the memory. Lavoisier began the systematic system of nomenclature used today.

The names of many of the elements have been given in Chapter 12. The system of naming compounds is designed to supply information concerning the substances involved. The name of a compound often tells the names of the constituent elements. This information, coupled with a knowledge of valence, can be used to write a possible formula with all that it implies. The nomenclature of chemistry is, in this respect, superior to the naming method used in any of the other sciences.

The use of "-ide". When a compound consists of two elements, its name ends in "-ide". Thus zinc chloride refers to a compound of zinc and chlorine. Applying a knowledge of valence, the chemist establishes its formula as ZnCl_2 . In naming compounds of two elements (binary

compounds), it is conventional to name the metal first. Oxides, bromides, iodides, and sulphides are examples of compounds in this group.

"Peroxides" such as hydrogen peroxide (H_2O_2), sodium peroxide (Na_2O_2), and barium peroxide (BaO_2) are unusual oxides possessing formulae that do not appear to conform to valence rules. They possess one more atom of oxygen per molecule than is present in the normal



International Nickel

Fig. 14.1. John Dalton (1766–1844), an English school teacher, formulated the chemical atomic hypothesis.

oxide. If the formulae of the three peroxides listed be rewritten as ($\text{H}_2\text{O.O}$), ($\text{Na}_2\text{O.O}$) and (BaO.O), the valence relationship is more apparent.

The use of “-ous” and “-ic”. When two elements unite in different proportions to form two different compounds, the suffixes “-ous” and “-ic” are used to distinguish these compounds. The suffix “-ous” denotes the lower valence. Since mercury has the two valences, one and two, mercurous oxide would be the name of the compound whose formula is Hg_2O . and mercuric oxide would be the name of the compound with the formula HgO . Ferrous sulphide, formula FeS , is quite

different from ferric sulphide, Fe_2S_3 , although each consists of only iron and sulphur. Sometimes, in naming a compound, the endings “-ous” and “-ic” are ignored and another method indicating the relative number of atoms is used. P_2O_3 is the formula for phosphorous oxide or phosphorus trioxide, and P_2O_5 is the formula for phosphoric oxide or phosphorus pentoxide. Other examples are carbon monoxide (CO), carbon dioxide (CO_2), sulphur dioxide (SO_2), and sulphur trioxide (SO_3).

A recently devised system, rapidly gaining in popularity, places the valence of the element in Roman numerals immediately after the name of the element having the variable valence. For example, mercurous oxide becomes mercury I oxide, and mercuric oxide becomes mercury II oxide; ferrous sulphide becomes iron II sulphide, and ferric sulphide becomes iron III sulphide.

The formulae of some acids. Naming compounds, consisting of three elements, depends on a knowledge of the names of the more common acids. The formulae of these acids should be memorized:



Sulphuric acid

Nitric acid

Carbonic acid

Chloric acid

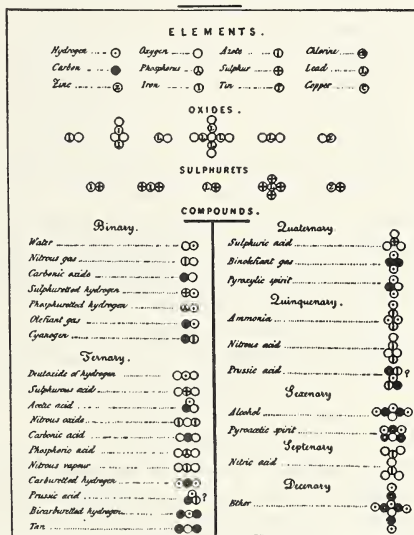
Phosphoric acid

ATOMIC SYMBOLS

John Dalton, D.C.L., F.R.S., &c.
explanatory of a

LECTURE

given by him to the MEMBERS of the
Manchester Mechanics' Institution,
October 19th 1835.



Corning Glass

Fig. 14.2. Some of the symbols used by Dalton, and the names and formulae of a number of compounds known in 1835.

The formulae of these acids should be memorized:

this reason they are known as **oxy-acids**. The properties distinguishing them as acids will be studied later. Chlorine, oxygen, and hydrogen combine to form four oxy-acids. These with their formulae are:

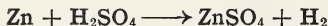
Chloric acid	HClO_3
Chlorous acid	HClO_2
Hypochlorous acid	HClO
Perchloric acid	HClO_4

The following system of naming is sometimes used whenever there is more than one oxy-acid containing the same three elements. The most important acid, or the one first discovered, is named the “-ic” acid. When there is one oxygen atom less in the molecule than in the “-ic” acid, the suffix “-ous” is substituted in the acid name. If there are two oxygen atoms fewer in the molecule than in the “-ic” acid, the prefix “hypo” is used along with the suffix “-ous”, e.g. **hypochlorous** acid. If there is one atom of oxygen per molecule more than in the “-ic” acid, the prefix “per-” is used along with the suffix “-ic”. Thus the importance of memorizing the formulae of the “-ic” acids is now apparent. HNO_2 is the formula of nitrous acid, and H_2SO_3 the formula of sulphurous acid. However, the system outlined above does not always apply accurately, e.g. it could not apply in naming the thirteen oxy-acids of sulphur.

To find the name of an acid of given formula, it is necessary to begin with the “-ic” acid and apply the rule. What is the name of the acid whose formula is H_3PO_2 ? H_3PO_4 is the formula of phosphoric acid. H_3PO_2 has two atoms of oxygen fewer per molecule than the “-ic” acid. Therefore, it is the formula of **hypophosphorous** acid.

Radicals. The formulae of the following compounds show remarkable similarity: H_2SO_4 , ZnSO_4 , Na_2SO_4 , CaSO_4 , CuSO_4 , PbSO_4 , $\text{Al}_2(\text{SO}_4)_3$, BaSO_4 , K_2SO_4 , MgSO_4 .

In each of the above compounds, the sulphur and oxygen atoms are found in the proportion of one to four. In the reaction represented by the equation



the SO_4 group leaves the molecule of sulphuric acid to reappear in a molecule of zinc sulphate. The SO_4 group is called the **sulphate radical**. It is present in many compounds and is capable of passing without change into and out of compounds.

A radical is a group of atoms acting as a single “unit” and having a definite valence. In H_2SO_4 , one “unit (SO_4)” is combined with two atoms of hydrogen. The valence of the sulphate radical is therefore

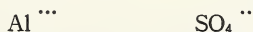
two, or it is divalent. The names of radicals derived from **-ic** acids are suffixed **-ate**. Radicals from **-ous** acids are suffixed **-ite**, e.g. the sulphite radical (SO_3) is derived from H_2SO_3 .

Learning the acid radicals and their valences presents little difficulty once the **-ic** acids and the system of nomenclature have been memorized. Here are a few of them.

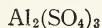
ACID RADICALS AND VALENCES

ACID FORMULA	RADICAL	NAME OF RADICAL	VALENCE OF RADICAL	FORMULA OF SODIUM SALT
H_2SO_4	SO_4	Sulphate	2	Na_2SO_4
H_2SO_3	SO_3	Sulphite	2	Na_2SO_3
HClO_3	ClO_3	Chlorate	1	NaClO_3
HClO	ClO	Hypochlorite	1	NaClO
HNO_3	NO_3	Nitrate	1	NaNO_3
H_3PO_4	PO_4	Phosphate	3	Na_3PO_4
H_2CO_3	CO_3	Carbonate	2	Na_2CO_3

The naming of salts. A salt forms when a metal replaces the hydrogen of an acid (Chapter 16). A salt derives its name from the metal and the acid radical, e.g. the sodium salt of sulphuric acid is called sodium sulphate, and the sodium salt of sulphurous acid is called sodium sulphite. The formulae of many salts can now be written. To write the formula of aluminum sulphate, it is first necessary to write the symbol and the radical with their valences.



Applying the rule of inverse valences, the formula is written



The naming of salts is dealt with more fully in Chapter 16.

Other radicals. Nitrogen and hydrogen occur in the proportion of one to four atoms, respectively, in many compounds. NH_4Cl is the formula of ammonium chloride. Because the radical NH_4 behaves like a metal in that it replaces metals and hydrogen in many reactions, like metals it is given a name ending in **"um"**. Since chlorine has a valence of one (HCl), the valence of the **ammonium** radical is one (NH_4Cl).

Hydroxides contain the radical OH having a valence of one and called the **hydroxyl radical**. Thus, the formula for sodium hydroxide is NaOH . Other common hydroxides are potassium hydroxide (KOH), calcium hydroxide ($\text{Ca}(\text{OH})_2$), and ammonium hydroxide (NH_4OH). Note that some ammonium and all hydroxide compounds, although

consisting of three elements, have names ending in “-ide”. This is understandable when it is remembered that a radical acts as if it were a single element.

EXERCISE

1. What is meant by chemical nomenclature?
2. What scientist is credited with beginning the systematic nomenclature used in modern chemistry?
3. What is the suffix used in naming compounds containing only two elements?
4. What is the rule that distinguishes between the suffixes *-ous* and *-ic* in distinguishing the compounds of elements that display variable valence?
5. Name the compounds whose formulae are FeS and Fe_2S_3 . Explain the significance of the suffix used in each case.
6. Name and write the formulae for the chlorides of copper, mercury, iron, phosphorus, arsenic, antimony, and tin.
7. Write the formula for each substance named in the following list. In each case put down the symbols for the elements involved and indicate their valences. Then establish a correct formula.

Sodium oxide, potassium iodide, silver sulphide, mercurous oxide, mercuric oxide, lead sulphide, barium chloride, barium sulphide, calcium bromide, cuprous oxide, cupric oxide, magnesium bromide, zinc oxide, hydrogen oxide, aluminum carbide, phosphorous chloride, phosphoric oxide, magnesium nitride, arsenious bromide, arsenic sulphide, calcium hydride, antimonious sulphide, antimonic oxide, silver oxide, ferrous oxide, ferric sulphide, stannous chloride, stannic oxide.

(Note: In the formation of sulphides, sulphur has a valence of two, since it behaves as a non-metal.)

8. Name the compounds represented by the following formulae. Recopy the formula in each case, establish and indicate the valences of the elements present, and then name the compound: ZnS , Na_2O , Na_2O_2 , FeO , FeCl_3 , Sb_2S_3 , Sb_2O_5 , CaCl_2 , BaO_2 , BaO , CuBr_2 , Hg_2O , HgCl_2 , H_2O , H_2O_2 , PBr_3 , P_2O_5 , As_2O_3 , As_2S_5 , H_2S , SnCl_4 , SnO .

9. (a) Give two possible names for each of the following compounds: P_2O_3 , P_2O_5 , PCl_3 , PCl_5 , As_2O_3 , As_2O_5 , AsBr_3 , AsBr_5 , Sb_2O_3 , Sb_2O_5 , Sb_2S_3 . (b) Name each of the following: SO_2 , SO_3 , CO , CO_2 .

10. What are the valences displayed by the elements which are combined with oxygen in the following oxides: H_2O , SO_2 , SO_3 , SiO_2 , Hg_2O , Fe_2O_3 , MnO_2 ?

11. While a knowledge of valence is of undoubted value to chemists, there are many well-known compounds whose formulae do not seem to be in accord with valence rules. What puzzling feature is revealed by each of the following: C_2H_2 (acetylene), CaC_2 (calcium carbide), Fe_3O_4 (magnetic iron oxide), Na_2O_2 (sodium peroxide), CO (carbon monoxide)?

12. In the naming of acids, explain the significance of the suffices, *-ic* and *-ous*, and of the prefixes *hypo-* and *per-*. Use the four oxy-acids of chlorine to illustrate your answer.

13. (a) Write the formulae for the following five common “oxy-acids”: nitric acid, chloric acid, sulphuric acid, carbonic acid, phosphoric acid. (b) Why is the memorization of the formulae of these five acids an imperative assignment?

14. (a) What is a "radical"? Give three examples. (b) Can radicals exist in a free condition? (c) Name the following radicals: (NO_3) , (ClO_3) , (SO_4) , (CO_3) , (PO_4) . (d) From a knowledge of the acids listed in Question 13, deduce and designate the valence of each of the radicals listed in (c).

15. Knowing that radicals derived from *-ous* acids are suffixed *-ite*, and that those derived from *-ic* acids are suffixed *-ate*, complete the accompanying table. Recopy the table in your note-book. Do not attempt to complete it in the text itself.

OXY-ACIDS OF CHLORINE			THEIR SODIUM SALTS	
Names	Formulae	Radicals	Names	Formulae
..... acid	. . .	(. .)	Sodium	. . .
..... acid	. . .	(. .)	Sodium	. . .
Chloric acid	HClO_3	(ClO_3)	Sodium chlorate	NaClO_3
..... acid	. . .	(. .)	Sodium	. . .

16. (a) Write formulae for the following acids: nitric, nitrous, phosphoric, phosphorous, hypophosphorous, sulphuric, sulphurous, carbonic. (b) Name the following radicals: (NO_3) , (NO_2) , (PO_4) , (PO_3) , (PO_2) , (SO_4) , (SO_3) , (CO_3) . (c) Recopy the radicals listed in (b) and knowing the formula of the acid from which each radical was derived, deduce and designate the valence of each radical listed. (d) Write the names and formulae of the calcium salts of all the acids listed in (a).

17. The rare element tellurium (Te) forms an acid which resembles sulphuric acid and is named telluric acid (H_2TeO_4). Write the formulae and names of the salts of this acid with potassium, silver, magnesium, aluminum, and iron.

18. Occasionally a less common radical is encountered such as the acetate radical ($\text{C}_2\text{H}_3\text{O}_2$). If this radical is derived from acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), what is its valence? Write formulae for the acetates of sodium, lead, zinc, and aluminum.

19. Aqueous solutions of certain gases such as hydrogen chloride, hydrogen bromide, hydrogen iodide, hydrogen fluoride and hydrogen sulphide display acid properties and the two-element acids formed, containing hydrogen and one other element are named (*hydro—ic*) acids. Name the acids having the formulae HCl , HBr , HI , HF , H_2S .

20. (a) What is the hydroxyl radical? What is its valence? (b) Write the formulae for the hydroxides of the following metals: sodium, potassium, magnesium, calcium, zinc, aluminum, and iron.

21. (a) What is the ammonium radical? Its valence? (b) Write the formulae for the following ammonium compounds: ammonium chloride, ammonium sulphide, ammonium sulphate, ammonium nitrate, ammonium phosphate, ammonium hydroxide, ammonium carbonate.

22. Write the names and formulae for two sulphates of each of the following: iron, mercury, and tin.

23. Write the formulae of the oxides, chlorides, nitrates, sulphates, sulphides, and phosphates of silver, calcium, aluminum, and mercury.

24. Write formulae for the following substances: magnesium sulphate, calcium carbonate, sodium chlorate, potassium nitrate, aluminum phosphate, sodium nitrite, silver carbonate, zinc sulphite, calcium phosphite, potassium

perchlorate, potassium hypochlorite, ammonium carbonate, ferrous sulphate, ferric sulphate, barium nitrate, oxygen gas, hydrogen gas, nitrogen gas, sodium chlorite, zinc oxide, zinc hydroxide, barium sulphide, potassium sulphite, aluminum sulphate, mercurous chloride, lead chlorite, silver chlorate, mercuric nitrate.

25. Write the names for the substances represented by the following formulae: KCl , Na_2O , K_2SO_4 , NaClO , H_3PO_2 , As_2O_5 , $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, NH_3 , P_2O_3 , PBr_5 , AlPO_4 , Ag_2O , BaO , BaO_2 , $(\text{NH}_4)_2\text{CO}_3$, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, MgSO_3 , N_2 , $\text{Ca}(\text{ClO}_3)_2$, NH_4OH , SO_3 , FeS , CO , Na_2SO_3 , SO_2 , K_2S , CO_2 , CS_2 , CCl_4 , HClO_4 , SnCl_4 , KNO_2 , Na_2O , Na_2O_2 , H_2O_2 , $\text{Ca}_3(\text{PO}_4)_2$, $\text{Fe}(\text{NO}_3)_3$, Cu_2S , CuBr_2 , CuBr , SiO_2 , Mg_3N_2 , Fe_2O_3 , Fe_3O_4 , FeO , HClO , Sb_2S_3 , NaClO_3 , NaBrO_3 , KIO_3 .

26. Correct the following formulae by correcting or supplying the necessary subscript numbers wherever necessary: Na_2PO_4 , MgBr , Zn_2S_2 , PO_5 , $\text{Al}(\text{OH})_2$, AgCl_2 , CaCl , AlO_3 , Mg_2CO_3 , ZnOH_2 , $(\text{NH}_4)_2\text{Cl}$, Ca_2SO_4 , $\text{Al}_3(\text{SO}_4)_2$, KPO_4 , $\text{Ag}(\text{NO}_3)_2$, NaS , $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)$, AlCl , AsCl_2 , $(\text{NH}_4)\text{PO}_4$, KO , Fe_3S_2 .

CHAPTER 15

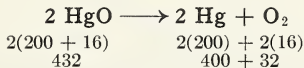
Using Equations

... Nature's great book is written in mathematical language.

GALILEO

Every manufacturer is vitally concerned not only with the kinds of raw materials used and the finished products obtained, but also with the relative quantities, and hence with the relative costs of raw and finished goods. If the chemist is to do any **quantitative** work in the laboratory, or in chemical industry, he requires a complete understanding of the processes involved, and a command of chemical equations and calculations. There is no fumbling or guessing in the chemical industry. Every chemical equation represents in concise form, both qualitatively and quantitatively, facts learned by experiment, having reference to the changes undergone and to the relative quantities of the materials involved. Equations do not usually indicate whether the reaction is endothermic or exothermic, whether a catalyst has been used, or what kind of apparatus or treatment is necessary. However, equations do express the relative quantities of the reacting substances and make possible the calculation of the proportions by weight and by volume of the substances involved.

Calculating relative weights. The decomposition of mercuric oxide by heat is represented by the following equation:

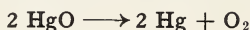


The numbers shown under the equation may represent grams, ounces, pounds, or any other units of weight. To prepare 400 pounds of mercury would require 432 pounds of mercuric oxide; to prepare one half of this amount of mercury, viz. 200 pounds, would require one half of the above weight of mercuric oxide, or 216 pounds. To prepare 100 grams of mercury would require $\frac{1}{4} \times 432 = 108$ gm. mercuric oxide.

Problem. What weight of oxygen could be produced from 40 gm. mercuric oxide?

Solution (by steps).

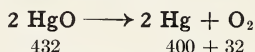
1. Write the equation for the reaction.



2. Decide (a) What is given (40 gm. mercuric oxide).

(b) What is to be found (weight of oxygen produced).

3. Indicate the relative weights of the substances reacting and select those concerned with the problem.



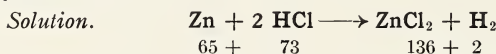
Thus, 432 gm. mercuric oxide would produce 32 gm. oxygen.

4. Solve the problem.

40 gm. mercuric oxide would produce $\frac{40}{432} \times 32$ gm. oxygen.

Weight of oxygen produced = 2.96 gm.

Problem. What weight of zinc chloride could be produced from 5 pounds of zinc?



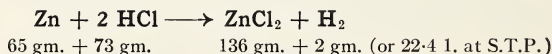
Thus 65 pounds of zinc would give 136 pounds of zinc chloride, and

5 pounds of zinc would give $\frac{5}{65} \times 136 = 10.46$ pounds of zinc chloride.

Solving weight-volume problems. Problems frequently involve both weights and volumes.

Problem. What volume of hydrogen, collected at S.T.P., could be produced from 130 gm. zinc?

Solution.



In solving this problem, the G.M.V. (22.4 l. at S.T.P.) is selected rather than the G.M.W. (2 gm.) because the problem asks for a *volume* of hydrogen.

65 gm. zinc liberate 22.4 l. of hydrogen at S.T.P.

130 gm. zinc liberate 44.8 l. of hydrogen at S.T.P.

Problem. What volume of oxygen at 10° C. and 740 mm. pressure could be obtained from 49 gm. potassium chlorate?



245 gm. potassium chlorate give 67.2 l. oxygen (S.T.P.)

49 gm. potassium chlorate give $\frac{49}{245} \times 67.2 = 13.44$ l. oxygen (S.T.P.)

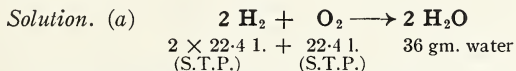
Volume of oxygen at 273° A. and 760 mm. is 13.44 litres.

Volume of oxygen at 283° A. and 740 mm. is

$$13.44 \times \frac{283}{273} \times \frac{760}{740} = 14.3 \text{ litres.}$$

Hence, 49 gm. potassium chlorate produce 14.3 l. oxygen at 10° C. and 740 mm. pressure.

Solving volume problems. *Problem.* (a) What volume of oxygen would be needed for the complete combustion of 44.8 l. hydrogen, both gases measured at S.T.P.? (b) What volume of oxygen at any temperature and pressure would be required for the complete combustion of 20 quarts of hydrogen measured at the same temperature and pressure?



44.8 l. hydrogen at S.T.P. require 22.4 l. oxygen at S.T.P.

(b) The volume relationship (2:1) in the above equation could apply to other units of volume than litres, and to other conditions of temperature and pressure if both gases are measured at the same temperature and pressure.

Hence 2 volumes of hydrogen require 1 volume of oxygen if both are measured at the same temperature and pressure.

And 20 quarts of hydrogen would require 10 quarts of oxygen if both are measured at the same temperature and pressure.

EXERCISE

A

I. In the work covered in the previous chapters, a large number of word equations have been studied covering a wide variety of chemical changes.

Write balanced equations to represent correctly the following reactions. For each reaction write (a) a "word equation" for the chemical change involved; (b) a "skeleton equation"; (c) a final "balanced equation."

- Mercury is heated in air.
- Mercuric oxide (red oxide of mercury) is strongly heated.
- Potassium chlorate is decomposed by heating.
- A mixture of potassium chlorate and manganese dioxide is heated.
- Water is added to sodium peroxide.
- A freshly-scraped piece of iron becomes tarnished.

7. (a) Sulphur burns in a jar of oxygen. (b) The product in (a) is dissolved in a small quantity of water.
8. (a) Carbon (charcoal) burns in a jar of oxygen. (b) The product is dissolved in water.
9. (a) Yellow phosphorus burns in a jar of oxygen. (b) The product is dissolved in water.
10. (a) Sodium burns in a jar of oxygen. (b) The product is dissolved in water.
11. (a) Magnesium burns in oxygen. (b) The product is dissolved in water.
12. (a) Calcium burns in a jar of oxygen. (b) The product is dissolved in water.
13. Finely divided iron is burned in a jar of oxygen.
14. The aluminum foil in a photoflash lamp is ignited.
15. Moist steel wool rusts.
16. A solution of sodium nitrite is allowed to drip slowly into a hot solution of ammonium chloride.
17. Nitrogen gas combines with hydrogen gas.
18. A piece of sodium is placed on cold water.
19. A piece of potassium is placed on cold water.
20. Metallic calcium is dropped into a beaker of water.
21. Finely divided magnesium is placed in boiling water.
22. Steam is passed through a heated tube containing finely divided iron.
23. Pieces of granulated zinc are placed in dilute sulphuric acid.
24. Granulated zinc is placed in dilute hydrochloric acid.
25. (a) Magnesium reacts with dilute sulphuric acid. (b) Aluminum reacts with dilute sulphuric acid. (c) Iron reacts with dilute sulphuric acid.
26. The three metals mentioned in the preceding question are allowed to react separately with dilute hydrochloric acid.
27. Steam is passed over highly-heated coke.
28. Dry hydrogen gas burns quietly from a jet.
29. A mixture of hydrogen and air explodes with a characteristic "pop".
30. Heated cupric oxide (black copper oxide) is reduced by a current of dry hydrogen.
31. Heated ferric oxide is reduced by dry hydrogen gas.
32. A mixture of hydrogen and chlorine gases is exposed to direct sunlight.
33. Hydrogen unites with molten sulphur.
34. Hydrogen (in the presence of a suitable catalyst) reacts with nitrogen.
35. A substance containing water is added to anhydrous copper sulphate and the solution is evaporated.
36. The dehydration of bluestone crystals.
37. (a) Washing soda crystals effloresce. (b) "Hypo" crystals are exposed to the dry air of the laboratory.
38. The electrolysis of acidulated water.
39. A mixture of hydrogen and oxygen gases are exploded in a eudiometer.
40. A solution of silver nitrate is mixed with a common salt solution.
41. Solutions of lead nitrate and potassium iodide are mixed.
42. A mixture of iron filings and flowers of sulphur is heated.

II. The following "skeleton equations" are correct, but unbalanced. This exercise is designed solely to give practice in the art of balancing equations.

Recopy the equation in each case and balance each equation by changing, where necessary, the coefficients of the formulae involved.

1.	Al_4C_3	$+ \text{H}_2\text{O}$	$\longrightarrow$	$\text{Al}(\text{OH})_3$	$+ \text{CH}_4$		
2.	AsCl_3	$+ \text{H}_2\text{S}$	$\longrightarrow$	As_2S_3	$+ \text{HCl}$		
3.	FeCl_3	$+ (\text{NH}_4)_2\text{S}$	$\longrightarrow$	Fe_2S_3	$+ \text{NH}_4\text{Cl}$		
4.	NaOH	$+ \text{H}_3\text{PO}_4$	$\longrightarrow$	Na_3PO_4	$+ \text{H}_2\text{O}$		
5.	Na_2CO_3	$+ \text{H}_3\text{PO}_4$	$\longrightarrow$	Na_3PO_4	$+ \text{H}_2\text{O}$	$+ \text{CO}_2$	
6.	KOH	$+ \text{SO}_2$	$\longrightarrow$	K_2SO_3	$+ \text{H}_2\text{O}$		
7.	$\text{C}_{10}\text{H}_{16}$	$+ \text{Cl}_2$	$\longrightarrow$	HCl	$+ \text{C}$		
8.	KMnO_4	$+ \text{H}_2\text{SO}_3$	$\longrightarrow$	K_2SO_4	$+ \text{MnSO}_4$	$+ \text{H}_2\text{SO}_4$	$+ \text{H}_2\text{O}$
9.	MnO_2	$+ \text{HCl}$	$\longrightarrow$	MnCl_2	$+ \text{H}_2\text{O}$	$+ \text{Cl}_2$	
10.	KClO_3	$+ \text{HCl}$	$\longrightarrow$	KCl	$+ \text{H}_2\text{O}$	$+ \text{Cl}_2$	
11.	CaC_2	$+ \text{H}_2\text{O}$	$\longrightarrow$	$\text{Ca}(\text{OH})_2$	$+ \text{C}_2\text{H}_2$		
12.	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	$+ (\text{NH}_4)_2\text{S}$	$\longrightarrow$	PbS	$+ (\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_2$		
13.	Al	$+ \text{H}_2\text{SO}_4$	$\longrightarrow$	$\text{Al}_2(\text{SO}_4)_3$	$+ \text{H}_2\text{O}$	$+ \text{SO}_2$	
14.	Al	$+ \text{NaOH}$	$\longrightarrow$	Na_3AlO_3	$+ \text{H}_2$		
15.	KNO_3		$\longrightarrow$	KNO_2	$+ \text{O}_2$		
16.	NaI	$+ \text{MnO}_2 + \text{H}_2\text{SO}_4$	$\longrightarrow$	Na_2SO_4	$+ \text{MnSO}_4$	$+ \text{H}_2\text{O}$	$+ \text{I}_2$
17.	KOH	$+ \text{Cl}_2$	$\longrightarrow$	KClO_3	$+ \text{KCl}$	$+ \text{H}_2\text{O}$	
18.	$\text{Al}_2(\text{CO}_3)_3$	$+ \text{H}_2\text{O}$	$\longrightarrow$	$\text{Al}(\text{OH})_3$	$+ \text{H}_2\text{O}$	$+ \text{CO}_2$	
19.	FeS_2	$+ \text{O}_2$	$\longrightarrow$	Fe_2O_3	$+ \text{SO}_2$		
20.	Na_2CO_3	$+ \text{FeCl}_3 + \text{H}_2\text{O}$	$\longrightarrow$	$\text{Fe}(\text{OH})_3$	$+ \text{NaCl}$	$+ \text{CO}_2$	

III. A student is asked to write a balanced equation for the "decomposition of potassium chlorate when heated." Because this student does not possess a sound knowledge of this experiment, he does not attempt to write a correct "sentence equation", and instead tries to predict the outcome algebraically. Some of his attempts are listed as follows: (a) $\text{KClO}_2 \longrightarrow \text{KCl} + \text{O}_2$; (b) $\text{KClO} \longrightarrow \text{KCl} + \text{O}$; (c) $2 \text{KClO}_3 \longrightarrow 2 \text{K} + \text{Cl}_2 + 3 \text{O}_2$; (d) $\text{KClO}_3 \longrightarrow \text{KCl} + \text{O}_3$.

Analyze his errors in each attempt.

This same student's notebook reveals the following errors in attempting to answer some of the equations covered in Part (A): (a) $\text{Mg} + \text{O} \longrightarrow \text{MgO}$; (b) $\text{Cu} + \text{O}_2 \longrightarrow \text{CuO}_2$; (c) $\text{Zn} + \text{HCl} \longrightarrow \text{ZnCl} + \text{H}$; (d) $\text{Ca} + \text{H}_2\text{O} \longrightarrow \text{CaOH} + \text{H}_2$.

Analyze his errors in each attempt.

B

I. Problems involving weight relationships only

1. What weight of oxygen could be produced from 100 gm. mercuric oxide?
2. What weight of oxygen could be produced from 100 gm. potassium chlorate?
3. What weight of mercuric oxide would be required to produce 50 gm. oxygen?
4. What weight of potassium chlorate would be required to produce 50 gm. oxygen?
5. What weight of aluminum chloride would be produced by the action of excess hydrochloric acid on 40 gm. aluminum?
6. How many pounds of zinc sulphate could be produced from 130 pounds of zinc?

7. What weight of water would be produced by the reduction with hydrogen of 35 gm. cupric oxide?

8. If 10 gm. sodium are dropped on water and the resulting solution is evaporated to dryness, what weight of sodium hydroxide would be produced?

9. Calculate the weight of magnesium oxide produced when 40 gm. magnesium are burned.

10. What weight of sulphur dioxide can be produced from the burning of 64 gm. sulphur?

11. One ton of anthracite coal containing 80% carbon is completely burned in air. Calculate the weight of carbon dioxide produced.

12. What weight of (a) oxygen and (b) hydrogen could be obtained by the electrolysis of 200 pounds of water?

II. Problems involving weight-volume relationships

1. What (a) weight and (b) volume of sulphur dioxide, measured at S.T.P., would be formed by the burning of 32 gm. sulphur?

2. If 10 gm. cupric oxide are reduced by dry hydrogen, (a) what weight of copper would be formed? (b) What weight and what volume of hydrogen at S.T.P. would be required?

3. Assuming that the equation



represents the chemical action taking place when steam is passed over heated iron, calculate the weight of iron necessary to produce 10 litres of hydrogen at S.T.P. What weight of iron oxide will be formed?

4. (a) What volume of oxygen measured at S.T.P. can be produced from 49 gm. potassium chlorate? (b) What volume would this oxygen occupy at 20° C. and 750 mm. pressure?

5. What volume of hydrogen measured at 23° C. and 748 mm. pressure can be produced from 40 gm. zinc?

6. What weight of zinc will be required to produce 520 cc. of hydrogen measured at 25° C. and 764 mm. pressure?

7. What volume of hydrogen at 40° C. and 690 mm. pressure could be obtained by the action of excess hydrochloric acid on 8 gm. magnesium?

8. What volume of oxygen measured at 10° C. and 755 mm. pressure can be obtained by the electrolysis of 90 gm. water?

9. What volume of sulphur dioxide measured at 13° C. and 722 mm. pressure would be formed by the combustion of 8 gm. sulphur?

10. How many cubic feet of oxygen will be required for the complete combustion of 50 cubic feet of hydrogen if both gases are measured at the same temperature and pressure?

11. What volume of steam measured at 150° C. and 760 mm. pressure could be obtained by exploding 2 gm. hydrogen with excess oxygen?

12. On heating some potassium chlorate, 298 gm. potassium chloride were left. (a) What mass of chlorate was heated and (b) what volume of oxygen measured at 22° C. and 760 mm. pressure was formed?

CHAPTER 16

Ionization, Acids, Bases, and Salts

The theory that can absorb the greatest number of facts, and persist in doing so, generation after generation, through all changes of opinion and detail, is the one that must rule all observation.

JOHN WEISS

The electron theory explains electrovalence. It also accounts for the formation of positive and negative ions and these in turn explain the behaviour of metals and non-metals in chemical reactions. However, the theory of ionization was formulated long before the modern electron theory.

An electric current will pass through some solutions but not through others. Solutions of sulphuric acid, sodium hydroxide, and sodium chloride, for example, are all excellent conductors of electricity, whereas distilled water is a non-conductor, and alcohol and sugar (either in their pure state or in solution) do not conduct an electric current.

IONIZATION

To explain these differences in conductivity, Michael Faraday (1791-1867) incorrectly assumed that the electric current caused some substances to break up into electrified parts that he called ions. Substances forming ions, he said, would conduct electricity, and substances not forming ions would not conduct electricity. The former he called electrolytes and the latter non-electrolytes. This theory did not satisfy a Swedish student, Svante Arrhenius, because it failed to explain many reactions taking place in solution. After many years of study and experimentation, Arrhenius, in 1887, proposed what is known today as the **ionization theory** or the **theory of electrolytic dissociation**. He believed that electrolytes dissociated in solution *before* the electric current was passed through them, and that the ions were *not caused* by the electric current but that their existence could explain the conductivity of solutions.

Arrhenius' theory of ionization. Following is a summary of the ionization theory.

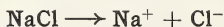
1. Electrolytes dissociate in solution to form electrified particles called **ions**.

2. Two kinds of ions are formed by this dissociation: positive and negative ions.

3. The number of positive charges is always equal to the number of negative charges on the ions, so that the solution of any electrolyte is always electrically neutral.

Some **electrolytes** can be melted, and in the molten state, without the presence of water, they will ionize and conduct an electric current.

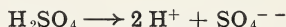
The nature of an ion. When sodium and chlorine combine to form sodium chloride, each sodium atom (Na^0) loses an electron and becomes a sodium ion (Na^+), and each chlorine atom (Cl^0) gains an electron and becomes a chloride ion (Cl^-). Sodium chloride is a solid and in this state the ions are held in fairly rigid position by their electrical attraction. If, however, sodium chloride is *dissolved in water*, its ions become freely *mobile*.



The above equation shows that solid sodium chloride forms two ions, one a sodium ion with a positive charge, and the other a chloride ion with a negative charge.

If an electric current is passed through this solution, the ions will move under the influence of the electrical charges on the electrodes.

A molecule of sulphuric acid, in ionizing, forms two hydrogen ions, each with a positive charge, and one sulphate ion with two negative charges.



Although sulphuric acid forms twice as many positive as negative ions, the numbers of positive and negative *charges* are the same, so that a solution of sulphuric acid is electrically neutral. Note also that an ion is not necessarily a charged atom, but it may consist of a group of atoms (e.g. SO_4^{--}).

ELECTROLYSIS

The electrolysis of water with the formation of hydrogen and oxygen has already been described. This chemical reaction, together with the part sulphuric acid plays in it, can now be explained by reference to the theory of ionization.

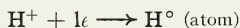
In water solution, sulphuric acid ionizes to give hydrogen ions and sulphate ions (see above). When an electric current is passed

through this solution, the hydrogen ions move towards the negatively charged cathode, and the sulphate ions move towards the positively charged anode.

In addition to the hydrogen ions and the sulphate ions there are a few hydrogen ions and hydroxyl ions resulting from the slight ionization of water (p. 214).



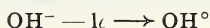
At the cathode, each positively charged hydrogen ion gains an electron and becomes an electrically neutral hydrogen atom.



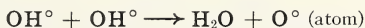
The hydrogen atoms then combine in pairs to form hydrogen molecules. These molecules accumulate and rise as bubbles of hydrogen gas from the cathode surface.



At the anode, there is a competition between the sulphate ion and the hydroxyl ion. Both of these ions are negatively charged and have a tendency to give up their electrons. However, the hydroxyl ion has a much greater tendency to give up electrons than has the sulphate ion (p. 215). Hence each hydroxyl ion gives up its charge (loses an electron) to become a neutral hydroxyl group.



Two neutral hydroxyl groups combine to form a molecule of water and an atom of oxygen.



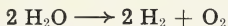
Two oxygen atoms then combine to form an oxygen molecule. As the molecules accumulate, they rise to the surface as bubbles of oxygen gas.



The excess of hydrogen ions left in the vicinity of the anode combines with the excess sulphate ions to form sulphuric acid.



As a result of this electrolysis, water is decomposed into hydrogen (two volumes) and oxygen (one volume).



The sulphuric acid produces a solution which conducts the current well enough to produce the electrolysis at each electrode.

Acids, bases and salts, are three types of compounds whose aqueous solutions are good electrolytes. These will now be studied in detail.

ACIDS

Occurrence. Acids are found in nature in the juices of many fruits. Citrus fruits such as lemons, oranges, and grapefruits, contain citric acid, and most unripe fruits such as apples, peaches, and plums are also acidic. The stems and leaves of some plants, e.g. rhubarb, also contain acids that give them their characteristic sour taste. In fact the word *acid* comes from a Latin word *acidus* meaning sour.



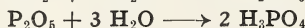
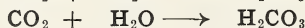
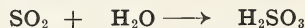
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Fig. 16.1. The bottle containing the hydrofluoric acid is made of the plastic polyethylene. Oxalic acid is a solid.

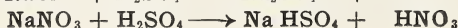
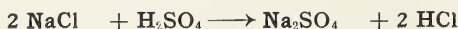
Bacteria cause the fermentation of fresh milk to produce a curdy mixture with a sour taste caused by the presence of lactic acid. The fermentation of "hard" apple cider by bacterial action produces another acid, named acetic acid, found in the cider vinegar so formed.

Carbonic acid and other organic acids are found in all natural waters, particularly where plant or animal remains have decomposed.

Preparation. Acids can be prepared by the reaction between acidic oxides (*acid anhydrides*) and water.



However, this is not the common commercial method of preparation. Most of the important acids are manufactured by *heating* their least expensive salts *with sulphuric acid*.



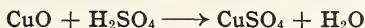
In each case the acid formed is separated from the reacting substances by methods based on differences in boiling points. The manufacture of sulphuric acid will be described later. Sometimes an acid can be prepared by *direct union* of the elements, e.g. chlorine and hydrogen will unite directly to form hydrogen chloride.

Properties. There are many thousands of known acids. Some of these are solids, some liquids, and a few are gases at ordinary temperatures.

During the electrolysis of any acid solution, hydrogen gas is always produced at the cathode, while the product or products obtained at the anode, depend on the acid electrolysed. The source of the hydrogen gas is the **hydrogen ion**, H^+ , and therefore all acids contain hydrogen ions. Indeed, some authorities go so far as to define the hydrogen ion as "the only acid" because the properties usually attributed to acids are in reality the properties of the hydrogen ion.

In addition to containing the hydrogen ion, all acids in *water solution* have the following properties:

1. They have a sour taste.
2. They affect indicators: (a) blue litmus is turned red, (b) pink phenolphthalein is turned colourless, and (c) neutral (green) bromthymol blue is turned yellow.
3. They react with some metals (see activity table, Chapter 6) to form hydrogen and a salt.
4. They react with the oxides of metals to form salts and water, e.g.

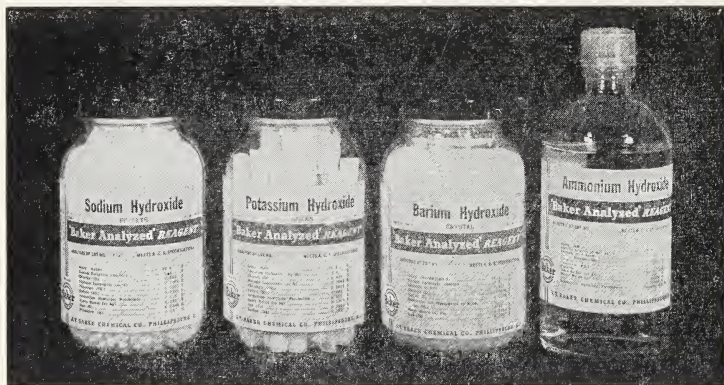


5. All solutions of acids neutralize bases.
6. Acids react with carbonates or bicarbonates to liberate carbon dioxide gas.

Strength. The strength of an acid depends upon the degree of ionization, or the concentration of the hydrogen ions, when the acid is dissolved in water. Hydrochloric acid is a better conductor of electricity and has greater chemical activity than acetic acid solution because it is more completely ionized than acetic acid. Nitric and sulphuric acids are also highly ionized in solution. Acids giving a high concentration of hydrogen ions are called *strong acids*. The following strong acids are listed in order of strength: hydrochloric, nitric, sulphuric, and phosphoric. *Weak* acids are poor ionizers, e.g. acetic, carbonic, and hydrosulphuric. *Concentration* and *strength* of acids should not be confused. A concentrated acid solution contains a high percentage of the acid molecules not necessarily freely ionizing; thus a concentrated solution of acetic acid is not as strong as a dilute solution of hydrochloric acid.

BASES

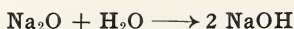
A typical base. Bases do not commonly occur in nature and are, therefore, probably not as familiar as acids. When sodium reacts with water, hydrogen and a compound called sodium hydroxide are formed. Sodium hydroxide is a typical base. Most metals react with oxygen



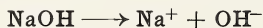
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Fig. 16.2. Four common hydroxides.

to form metallic oxides. The oxides of some metals react with water to form hydroxides, e.g.



When a metallic hydroxide, no matter how formed, is dissolved in water, it dissociates to give metallic ions and *hydroxyl* ions.

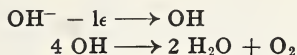


The properties usually attributed to bases are in reality the properties of the hydroxyl ion. Hence the hydroxyl ion may be considered as "the only base".

Properties. In addition to containing the hydroxyl ion, all bases in *water solution* have the following properties.

1. They have a bitter taste.
2. They feel slippery and soapy to the touch.
3. They affect indicators: (a) red litmus is turned blue, (b) colourless phenolphthalein is turned pink, and (c) neutral (green) bromthymol blue is turned blue.
4. They neutralize acids.

5. When an electric current is passed through a solution of a base, oxygen is formed at the anode.



Alkalis. Both sodium hydroxide and potassium hydroxide are very soluble in water, and both dissociate freely to give large quantities of hydroxyl ions. These two *strong bases* that exhibit marked chemical activity, including *caustic* and *corrosive* actions, are called **alkalis**. The preparation of lye or caustic soda is described in Chapter 23.

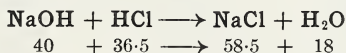
Other bases. *Calcium hydroxide*, commonly called **slaked lime**, is but sparingly soluble in water, and its solution, called **limewater**, is not as strongly basic as are the solutions of sodium and potassium hydroxides. It is cheaply made by the reaction between quicklime and water. *Ammonium hydroxide* is an important, although weak and unstable base. It is made by "dissolving" ammonia gas in water and exists only in solution. Efforts to evaporate this solution to obtain pure ammonium hydroxide result only in the unstable compound decomposing.



For this reason, ammonium hydroxide is sometimes called the volatile base.

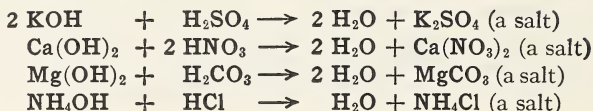
NEUTRALIZATION

When solutions of any base and any acid are mixed in the correct proportions, the distinctive properties of both disappear, and a *salt* and *water* are produced. As a result of this reaction, each is said to **neutralize** the other.



In the reaction represented by the above equation, solutions of sodium hydroxide and hydrochloric acid produce a neutral solution of common salt. That is, if 40 units by weight of sodium hydroxide in solution are mixed with a solution containing 36.5 units by weight of hydrogen chloride, the resulting solution will contain 18 additional units by weight of water, and 58.5 units by weight of salt and will not show any characteristic properties of either a base or an acid. **Neutralization** may be defined as the reaction of an acid with a base to form water and a salt. All neutralization reactions are exothermic.

Other examples of neutralization are:

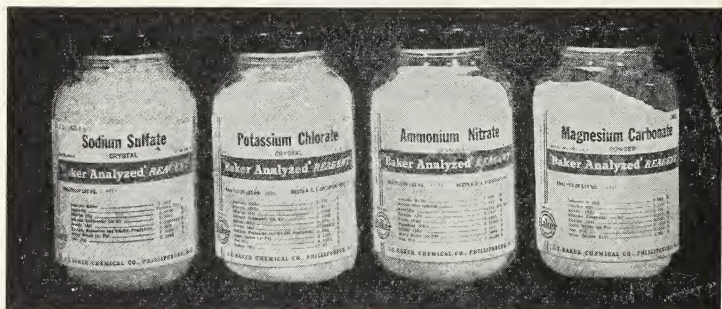


A knowledge of neutralization is useful in many situations. The destructive effect of acid burns can be minimized by a prompt application of a weak base, or if the burn has been caused by an alkali, the effect can be neutralized by the application of a weak acid such as vinegar. When material has been treated with an acid in industry, the excess acid is often "destroyed" with a weak base; an excess of base is removed by treatment with a weak acid. Acid soils, useless for growing most crops, are "sweetened" by the addition of slaked lime.

SALTS

A salt is a compound formed by the replacement of all or part of the available hydrogen of an acid molecule by either a metal or an electro-positive radical (e.g. ammonium). Salts are composed of the *positive part of a base* and the *negative part of an acid*.

It is almost impossible to list the general properties of salts because they crystallize in so many different solid geometric forms and show such marked variations in solubilities. Their colours also vary widely, e.g. common salt is white, copper sulphate (hydrate) is blue, potassium permanganate is dark purple, and lead iodide is yellow.



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Fig. 16.3. Four salts commonly found in the laboratory.

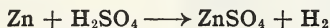
Occurrence. Salts abound in the earth and much of the earth's crust is composed of *insoluble salts*. Some examples of these are calcium carbonate, the main component of limestone, and many varieties of

silicates which occur in feldspars, micas, hornblende, talc, and clay. Soluble salts may occur in regions where there is little rainfall, or in underground deposits protected by layers of impervious rocks. Some of these are common salt, Chile saltpetre, potassium chloride, and magnesium sulphate.

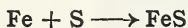
Although many salts used commercially occur in nature, many thousands are prepared by the chemist.

Preparation. There are various methods of preparation.

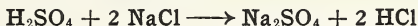
1. By neutralization (see above).
2. By the displacement of the hydrogen of an acid by a metal:



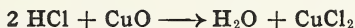
3. By the union of a metal and a non-metal:



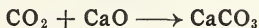
4. By the action of an acid on a salt of a more volatile acid:



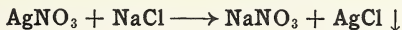
5. By the action of an acid on the oxide of a metal:



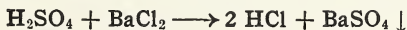
6. By the action of an acidic oxide (acidic anhydride) on a basic oxide (basic anhydride):



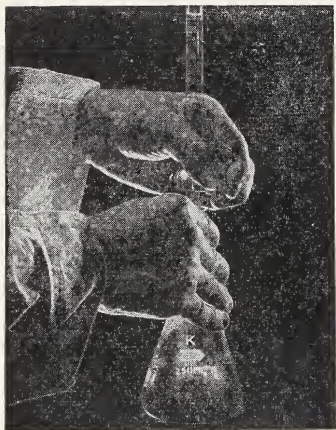
7. By "double decomposition" from two salts, or from an acid and a salt. This method makes impossible the separation of the two substances formed unless one of them is soluble and the other insoluble, e.g. if *solutions* of silver nitrate and sodium chloride are mixed:



The silver chloride, being insoluble, **precipitates** and can be separated from the solution by filtration. The sodium nitrate can be recovered by evaporating the filtrate to dryness. If an acid and a salt are used, an acid and a salt are formed, and if the salt is insoluble in the acid solution, it can be recovered by filtration:



Not all of the above methods of preparation apply for all salts, but in general a given salt may be prepared by at least three different methods.



Kimble Glass

Fig. 16.4. The proper method of using a burette in titrating. The exact amount of an acid required to neutralize a known amount of a base can be determined by this method.

Classes of salts. The nomenclature of salts has been discussed in Chapter 14. Salts are usually divided into three classes: normal salts, acid salts, and basic salts. When a metal (or the ammonium radical) replaces all the available hydrogen of an acid molecule, a **normal salt** is formed (e.g. sodium sulphate, Na_2SO_4). An **acid salt** may be considered as formed by the partial neutralization of an acid by a base, i.e. only part of the available hydrogen in the acid molecule has been replaced (e.g. sodium bisulphate, NaHSO_4). A **basic salt** may also be considered as formed by partial neutralization. It contains one or more hydroxyl radicals, e.g. basic lead carbonate or "white lead", $\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3$.

EXERCISE

A

1. State the three essential points in Arrhenius' theory of ionization.
2. Distinguish between electrolytes and non-electrolytes. Give three examples of each.
3. By reference to the theory of ionization, explain the electrolysis of water.
4. (a) Name five foods that contain acids. (b) Give three ways in which acids can be prepared in the laboratory.
5. (a) State seven properties common to water solutions of acids. (b) List four acids in order of strength.
6. Why is hydrochloric acid regarded as a strong acid and acetic acid as a weak acid?
7. (a) State seven properties common to water solutions of bases. (b) List four bases in order of strength.
8. (a) Explain the meaning of the term *neutralization*. (b) Name the two products that are formed in every neutralization.
9. How would you determine whether the soil in your garden is basic or acidic? If you find it strongly acidic, suggest how you would remedy the condition.
10. Suggest a method for treating burns caused by acids; for treating burns caused by alkalis.
11. Write the equations for the neutralization of the following acids and

bases, and name the salt formed in each case. (a) sulphuric acid and sodium hydroxide; (b) nitric acid and calcium hydroxide; (c) hydrochloric acid and potassium hydroxide; (d) phosphoric acid and ammonium hydroxide.

12. (a) Write the formulae for nitric, nitrous, sulphuric, and sulphurous acids. (b) Write the equations that represent the chemical reactions that would take place if potassium hydroxide were added to each of the four acids named in (a). Give the chemical names of the salts that would be formed.

13. (a) State five general methods for preparing salts. (b) Name the chemicals that could be used to prepare samples of each of the following salts: sodium chloride, potassium nitrate, calcium carbonate, ammonium phosphate and sodium sulphate. Write the equation for each of the above reactions.

B

1. A solution of sodium hydroxide is neutralized with a solution of sulphuric acid and the resulting mixture is evaporated to dryness. The residue weighs 35.5 gm. What weight of sodium hydroxide was present in the original solution?

2. How many grams of potassium hydroxide would be required to neutralize 7.3 grams of hydrochloric acid?

3. If a solution containing 50 pounds of pure sodium hydroxide is neutralized with hydrochloric acid, what weight of common salt would be obtained?

4. How many grams of a 20% solution of hydrochloric acid are necessary to react with a solution of sodium hydroxide to form a solution containing 50 grams of common salt?

5. How many tons of ammonium sulphate can be prepared by the action of ammonium hydroxide on 1200 pounds of a 60% sulphuric acid solution?

6. What weight of potassium hydroxide would be required to neutralize 100 cc. sulphuric acid solution containing 9.8 grams of H_2SO_4 per litre?

CHAPTER 17

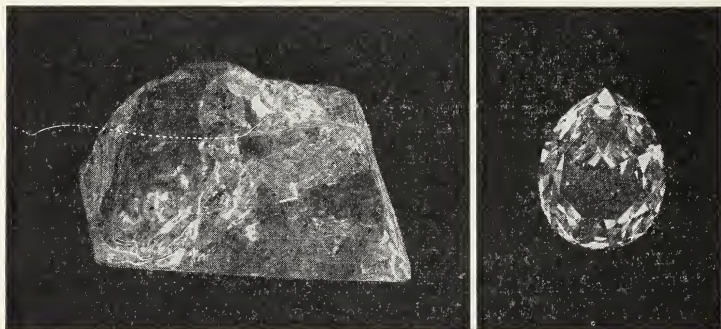
Carbon and Its Compounds

The chemists are a strange class of mortals who seek their pleasures among soot and flame, poisons and poverty; yet among all these evils I seem to live so sweetly that may I die if I would change places with the Persian King.

JOHN JOACHIM BECHER (1635-1682)

CARBON

Carbon has been chosen by nature as the foundation on which all living matter is built. Hence the number of *carbon compounds* exceeds the number of compounds of all the other elements combined. Yet it



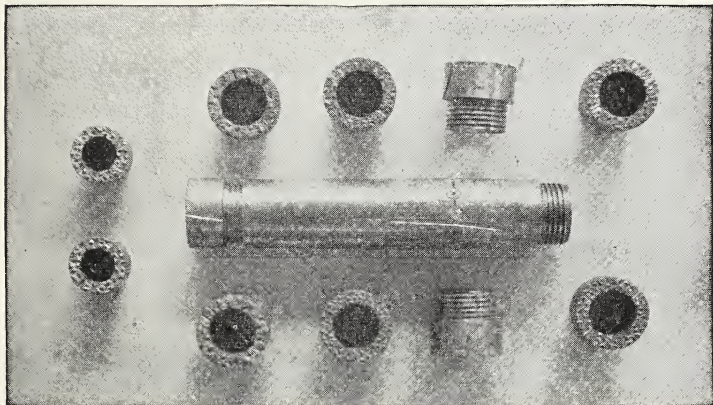
American Museum of Natural History

Fig. 17.1. Diamond. *Left*, a model of the world's largest diamond, the Cullinan, before cutting. *Right*, the Star of Africa, one of several gems cut from the original stone.

cannot be said that carbon is an abundant element. In spite of its indispensability to all forms of life, carbon is relatively scarce, comprising only 0.03% by weight of the earth's elements.

Occurrence. Carbon occurs in nature in both the free and the combined state. It is found as the element in **diamond**, **graphite**, and the many varieties of **coal**. Its compounds are found in all animal and plant tissues, and in the products obtained from these sources, e.g. foods, oils, wood, paper, cotton, wool, etc. Natural gas and petroleum

are natural sources rich in carbon, and each consists of a mixture of hydrocarbons. Another important natural compound of carbon is calcium carbonate, found in three forms, limestone, chalk, and marble. Other metallic carbonates are found but sparingly. Carbon dioxide, an important component of air, is the source of the carbon contained in all animal and plant products. The chemical change whereby green plants produce carbohydrates from carbon dioxide and water is called **photosynthesis**. This action is the most important chemical reaction



Northern Miner

Fig. 17.2. Diamond bits with reaming shell. Each bit contains many embedded diamonds.

known, because it is the source of supply for our food, shelter, and clothing. So numerous and so important are the compounds of carbon, that they are grouped into a special branch of chemistry called **organic chemistry**, dealing solely with the study of carbon and its compounds.

Crystalline forms. Diamond. The diamond is the purest natural form of carbon. It is an eight sided, colourless, transparent crystal. However, impurities, in small quantity, will colour it red, blue, or even black. It is the hardest substance known, has a specific gravity of 3.52, is insoluble in all liquids, is quite brittle, and does not conduct electricity. Chemically, a diamond is inert, being unaffected even by strong acids or alkalis. It cannot be melted, but at about 900°C . it burns in air to form carbon dioxide only.

Diamonds are found chiefly in South Africa which yields 90% of the world's supply. They are found as coarse, somewhat rounded

pebbles embedded in blue clay deposits in the necks of extinct volcanoes. They occur also in Brazil, India, and the Belgian Congo.

The rarity and the beauty of a diamond explain its value as a gem. With an index of refraction of 2.47, the greatest refractive index of any known substance, and cut by experts so that its surface is made of many light-reflecting facets, the diamond shines with unusual brilliance. Gems are sold by weight, and the unit of weight, the **carat**,

is equal to 200 milligrams. The industrial value of diamonds is even greater than their ornamental value. Their extreme hardness makes them valuable as cutting edges in diamond rock drills, necessary in exploring the possibilities of a mining area. Diamonds are also used in cutting glass and for drawing wire to a fine thread. The metal filament in an electric lamp is made by drawing wire through a diamond die.



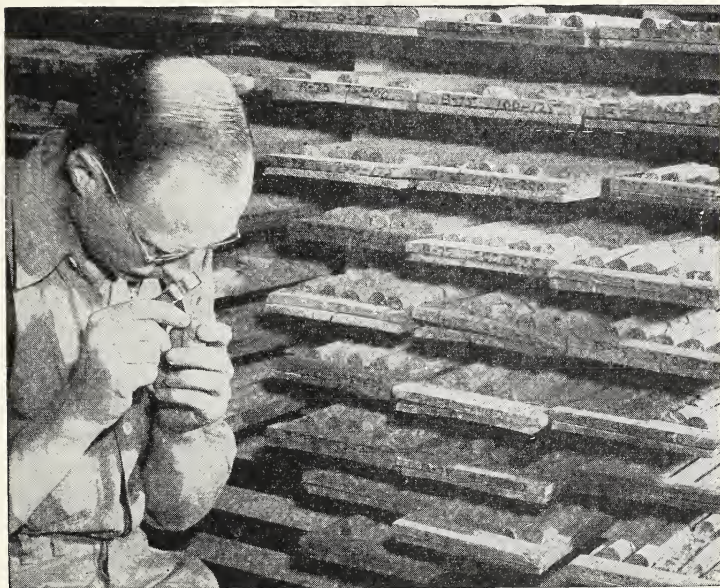
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Fig. 17.3. Diamond drilling. The diamond-bitted drills penetrate the hard rock for hundreds of feet. The drills bring up cores (samples of rock) that the geologists can read like a book.

Graphite. What a contrast to diamond is the form of carbon called graphite! Graphite, like diamond, is crystalline, but its grayish-black crystals are in very thin plates. The crystals are so soft and slippery they slide over one another with very little friction, thus making graphite an excellent lubricator.

Graphite is even more resistant to chemical action than diamond, and melting it is almost impossible. This inactivity makes graphite a useful ingredient in stove polish and acid-proof paints. Even at extremely high temperatures, graphite is not oxidized to any extent. This quality renders it valuable in manufacturing crucibles employed in the melting of metals. Graphite is a good conductor of electricity. This quality, coupled with its inactivity and high melting point, makes it useful as electrodes in electric furnaces and arc lamps. The only product of the combustion of burned graphite is carbon dioxide. The word "graphite" comes from the Greek *graphein* meaning "to write". Graphite, mixed with clay and baked, becomes the "lead" of lead pencils. The proportion of clay used determines the hardness of the lead; the more clay, the harder the pencil.

Graphite occurs in natural deposits in Ceylon, Siberia, Brazil, Mexico, Canada, and the United States, and has been formed by a continuation of the coal-forming process. It is manufactured at Niagara Falls, Ontario, by heating coke dust in an electric furnace. The coke dust is firmly packed, covered with sand, and raised to a very high temperature. At about $3,600^{\circ}\text{C}$. the carbon volatilizes



Northern Miner

Fig. 17.4. A geologist examining a core.

without melting, and when the gaseous carbon cools it sublimates as graphite.

Amorphous carbon. The word “amorphous” means without definite shape, hence not crystalline. Recent investigations with X-rays have shown that the so-called amorphous forms of carbon are composed of microscopic crystals something like the crystals of graphite. The principal amorphous forms, which are never quite pure, are charcoal, coke, boneblack, carbon black, and gas carbon.

Charcoal. If wood is heated in such a way that air is excluded, charcoal is formed. Wood is a mixture of many compounds, mostly made up of carbon, hydrogen and oxygen.

Heating the wood out of contact with air causes chemical reactions to take place with the resultant breaking down of the wood into simpler substances of which charcoal is one. Some of these substances can be separated by condensation. **Destructive distillation** is the decomposition of a complex substance, heated out of contact with air, and the condensation of the volatile products. Strongly heated wood gives off many gases. When cooled, some of these gases condense to form **wood tar** and a watery distillate known in the industry as

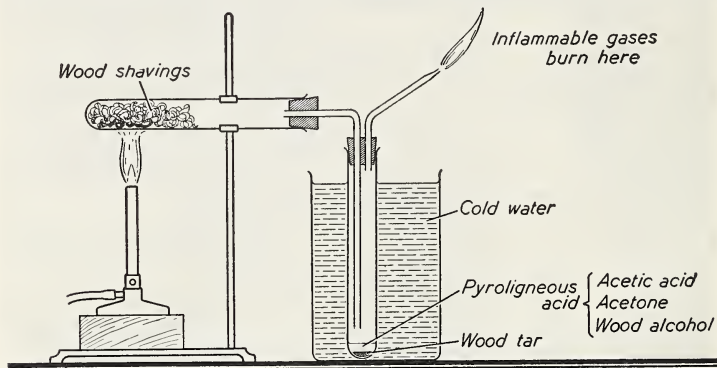
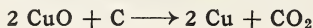


Fig. 17.5. The destructive distillation of wood.

pyroligneous acid. Wood tar is used to preserve wood. The watery distillate is a mixture of water, **acetic acid**, **acetone**, and **wood alcohol**. The gases that do not condense are inflammable, and can be used to heat the retorts containing the wood. They are a mixture of carbon monoxide, hydrogen, acetylene, methane, and some carbon dioxide.

Wood charcoal is a black, amorphous substance containing the salt impurities found in wood. Because of its porous nature, it floats on water. When the air is expelled from it by keeping it immersed for some time in boiling water, the charcoal, with a specific gravity of 1.7, sinks. Charcoal is insoluble in water and is not attacked by acids. It is an excellent fuel, burning without smoke or flame, and for this reason is sometimes burned in small stoves for cooking in the home, in railroad dining cars, or in peanut roasters. It burns in air to form carbon dioxide, leaving behind the impurities as mineral ash. Charcoal is a good reducing agent; when mixed with cupric oxide and intensely heated it produces copper and carbon dioxide:

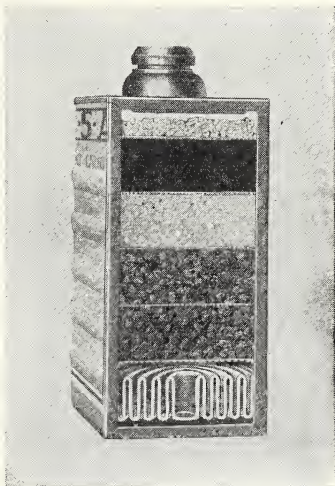


Activated charcoal. Activated charcoal is made by heating charcoal in a current of steam to remove all tarry impurities and gases, and then cooling it in a vacuum. Such charcoal has great adsorbing properties for gases and dissolved substances. **Adsorption** should be distinguished from absorption. In *absorption*, the liquid completely fills the tiny pores of the absorbing substance, e.g. the capillary action of blotting paper on ink. In *adsorption*, the pores are not filled, e.g. in adsorption by charcoal, the molecules of gas or dissolved material cling to the surface of the carbon atoms. Adsorption is a surface effect. Activated charcoal, made from compact substances such as cocoanut shells, peach, plum, or prune pits, is much more efficient for this purpose than that made from wood. The finer the grade of charcoal, the more numerous the pores, and hence the greater the surface area. Activated charcoal, when used in gas masks, will adsorb the most poisonous gases. Sometimes other chemicals are added to make the mask more efficient. Charcoal is also used to adsorb the foul-smelling gases from sewers or decaying flesh.

Boneblack. The destructive distillation of bones leaves a porous residue of boneblack, or **animal charcoal**, that is only about 15% carbon. Bone oil and pyridene are by-products found in the distillate.

Large quantities of boneblack are used in refining sugar. Hot, brown, impure sugar solution is poured through boneblack in large filters. The colouring matter is adsorbed by the boneblack, and from the clear solution, emerging as a filtrate, white sugar crystals are obtained.

Coke. The destructive distillation of soft coal results in many gases being given off and the residue remaining is coke. Industrially, soft coal is destructively distilled in huge iron retorts. When the mixture of emitted gases is cooled, **coal tar** and other oily products condense.



U.S. Bureau of Mines

Fig. 17.6. Cross section of a universal gas mask canister. The bottom layer is a cellulose filter for filtering toxic dusts, fumes, fogs, and smokes. The two layers above this contain activated charcoal for adsorbing most toxic gases. The dark layer near the top is *hopcalite*, a catalyst that converts carbon monoxide to carbon dioxide. The other layers are primarily to protect the hopcalite from moisture.

The remaining gases are washed, or “scrubbed”, by passing them through water to remove the **ammonia** gas. After removal of objectionable hydrogen sulphide by passing the gases through purifiers containing slaked lime or ferric oxide, the residual **illuminating gas**, composed mostly of hydrogen, methane, and carbon monoxide, is

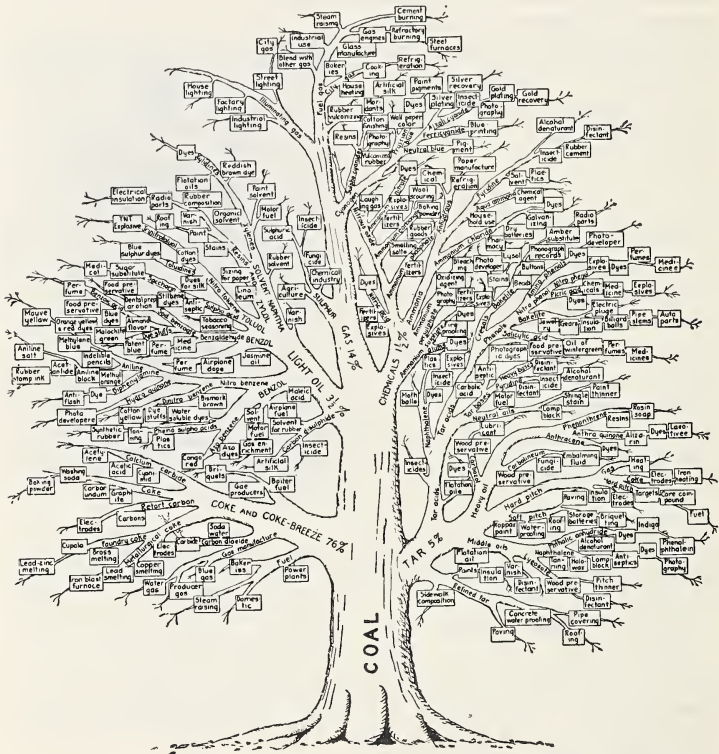


Fig. 17.7. Coal products tree. This shows the products obtainable from coal as a result of destructive distillation.

stored in large tanks and piped to homes and industrial plants, largely for fuel purposes. The residue of coke in the iron retorts is also valuable as a fuel. The reducing property of coke, however, is much more valuable to the chemist. Millions of tons of coke are used every year to extract iron, tin, and zinc from their ores. Coke is also used in the

manufacture of carbon disulphide, calcium carbide, an abrasive called carborundum, and a fuel called "water gas". A form of carbon, called "gas carbon", is also obtained from the walls of the retorts. This can be pressed into sticks and used for electrical purposes. Positive electrodes of dry cells are usually made from this form of carbon.

Carbon black. Carbon black is the most finely divided substance known to commerce, and the most intensely black. Each particle is so small it must be magnified 35,000 times to equal the size of a pinhead.

Carbon black is produced by two main processes, the **channel** method, and the **furnace** method, each of which involves the partial burning of hydrocarbons in a supply of air insufficient for complete combustion. The expensive channel method employs natural gas and produces a finer quality of "blacks", used principally for printing inks, paints, lithographic inks, carbon paper, and typewriter ribbons. Most of the carbon black produced by this method comes from Texas where natural gas is abundant. A single plant may consist of more than a hundred burner sheds stretched along an area 50 miles long and 5 miles wide. In such a plant five million flames burn day and night from fan-shaped burner tips placed only a few inches apart. Above the burners are rows of steel plates, or channels, 8 inches wide and 140 feet long. The luminous flames deposit layers of carbon on the cool steel, and the slow, back and forth movement of the channels results in their whole surface being covered. Stationary scrapers clean the carbon from the channels, and it drops to hoppers where a conveyor system moves it to the packing house.

The furnace method consists essentially of a combustion chamber, a cooling tower, an electrical precipitator, and several cyclone collectors. Natural gas is burned with a little air in the combustion chamber, and the hot gases, carrying the carbon black in suspension, are cooled and passed to the precipitator where the "black" is deposited. This method is flexible and therefore permits the production of the several varieties of "blacks" required by industry.

For easy handling, to reduce the space it occupies, to prevent contamination of the atmosphere, and to make it flow more easily, carbon black is pelletized into tiny beads that disintegrate very easily but are strong enough to pour like buckshot without creating a dust nuisance.

In addition to inks, paints, and lacquers, carbon black is now used in blackboards, metal polishes, fireworks, explosives, cosmetics, crayons, tarpaulins, waterproof sheeting, clothing, leather, paper, and even in some food preparations. However, 95% of all carbon black

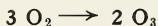
made is used in the rubber industry. Carbon black, in the rough proportion of 40% by weight of the crude rubber, greatly increases the life and mileage of tires, and prevents damage by oil and hardening in cold weather. More than a billion pounds of carbon black are produced annually.

Lampblack. Lampblack is manufactured by the incomplete combustion of oils, the carbon depositing as soot in a series of chambers. It is used in the production of printers' ink and black paint.

Allotropy. Many elements, among them carbon, sulphur, phosphorus, and oxygen, can exist in two or more forms with different physical, and almost identical chemical properties. These forms are known as **allotropes** and the elements existing in these forms are said to exhibit **allotropy**.

Diamond and graphite are the only allotropes of carbon. If one gram of either diamond or graphite is burned, exactly 3.67 gm. of carbon dioxide are produced. In 1893, Moissan dissolved graphite in molten iron in an electric furnace (3,000° C.), and rapidly cooled the iron in molten lead. When the outer layer of iron that resulted was dissolved in hydrochloric acid, many very small diamonds were discovered. If a diamond is heated out of contact with air, it is converted into graphite. This is another characteristic of allotropes, viz. each can be changed into the other form with no change in weight. The differences in properties of allotropes is possibly caused by the difference in the arrangement of the atoms in the molecule.

Oxygen exists in two forms. One of these is called oxygen (formula O_2), and the other, ozone (formula O_3). Ozone can be formed from oxygen by passing an electrical discharge through air or oxygen, or by exposing oxygen to ultra-violet light.



Ozone has a peculiar, pungent odour, sometimes noticeable after a thunder storm. It is a better and more effective oxidizing agent than oxygen.

CARBON DIOXIDE

Occurrence. It might be imagined that the enormous quantities of carbon dioxide used in photosynthesis would result in a deficiency of this gas in the air. This, however, is not the case, because large quantities of carbon dioxide are being continuously restored to the air by the breathing activities of animals and plants, by the burning of carbonaceous matter, and by the natural decomposition of animal and plant remains. Thus a balance is maintained, and the proportion

of carbon dioxide in the air remains approximately 3 parts in ten thousand. Carbon dioxide is given off by volcanoes, and it is also found in small quantities in some natural gases.

Carbon dioxide is also present in solution in all natural waters; in fact it is difficult to prepare water entirely free from it. The presence of carbon dioxide in natural waters makes possible the green plant life found therein, and which in turn is essential to all other aquatic life.

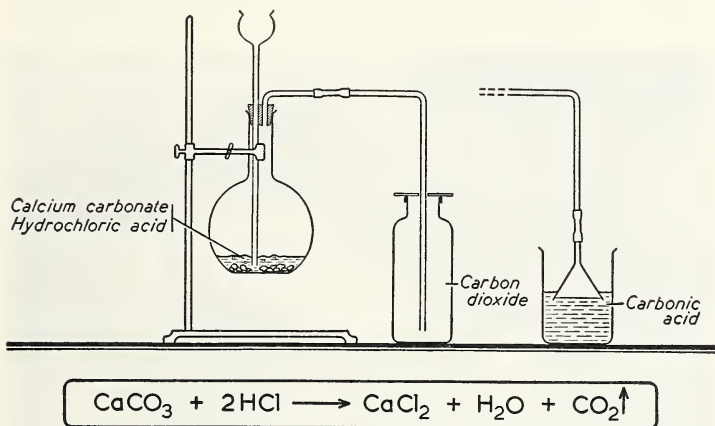
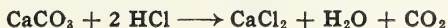


Fig. 17.8. The laboratory preparation and collection of carbon dioxide.

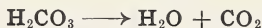
Preparation. About 1752, a Scottish chemist, Joseph Black, proved that expired air was not merely inspired air deficient in oxygen, but contained a "new" gas he named *fixed air*. Later, by heating chalk (a form of calcium carbonate) very intensely, he produced the same gas which he recognized by passing it through limewater and observing the same milky appearance visible when expired air was similarly tested. Lavoisier, using the scientific method (Chapter 3), proved this gas a compound of carbon and oxygen.

Carbon dioxide can be prepared in five different ways: by burning carbon or substances containing carbon; by decomposing a carbonate by heat; by the action of an acid on a carbonate; by respiration; and by fermentation.

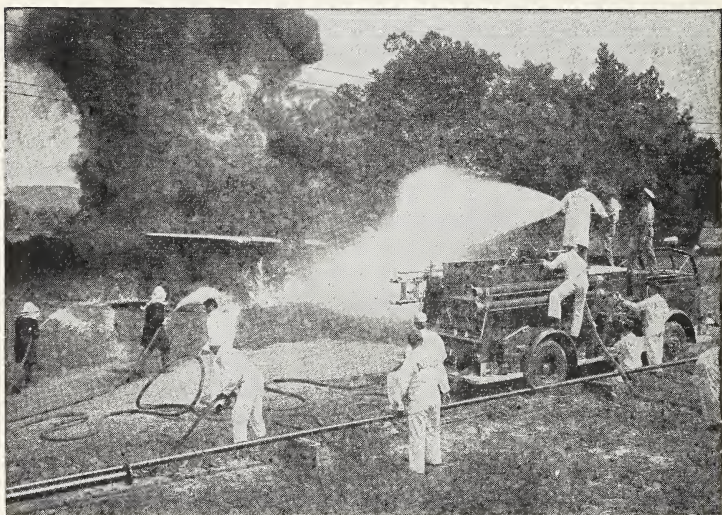
The usual laboratory method for preparing carbon dioxide is by the action of an acid on either a carbonate or a bicarbonate (Fig. 17.8):



The above reaction may be thought of as occurring in two steps. First, there is a double decomposition reaction producing calcium chloride and carbonic acid (H_2CO_3); this step is followed by the unstable acid decomposing to form water and carbon dioxide:



Properties. Carbon dioxide is a colourless and odourless gas. It can be easily liquefied by pressure, and, if the liquid carbon dioxide is cooled to -56.7°C. , it freezes (solidifies) to "dry ice". Carbon dioxide

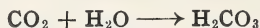


La France Fire Engine and Foamite

Fig. 17.9. Using liquid carbon dioxide to extinguish a fire. The carbon dioxide descends on the fire like snow. The two men on the left are using "air foam" to smother the spreading burning gasoline.

gas is somewhat soluble in water, and although some gas dissolves when collected by the downward displacement of water, the loss is not significant, and this is the convenient method of collection usually followed. However, it can be collected by the upward displacement of air as it is about one and one half times as dense as air (44 : 28.9).

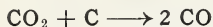
Carbon dioxide does not burn, nor does it support ordinary combustion. It is the anhydride of carbonic acid, i.e. it *reacts* with water to form carbonic acid:



Carbon dioxide will therefore turn moist blue litmus paper red, the gas combining with the water on the paper to form carbonic acid. Although it will not support ordinary combustion, carbon dioxide will continue to support the combustion of magnesium, if burning magnesium is plunged into it. A white ash, dotted with black specks, results:



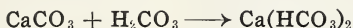
In this reaction, carbon dioxide is an oxidizing agent because it supplies the oxygen to oxidize the magnesium. Magnesium is the reducing agent. Carbon will also reduce carbon dioxide to carbon monoxide:



Carbon dioxide is the only gas capable of turning limewater milky. It reacts with calcium hydroxide to form a white precipitate of insoluble calcium carbonate.



If carbon dioxide continues to pass through the limewater and calcium carbonate mixture, however, the precipitate disappears and the solution becomes clear again. The calcium bicarbonate formed is soluble in water.



Uses. The properties mentioned above suggest many important uses. Because carbon dioxide is denser than air and does not support combustion, it is good for smothering fires. One of the most modern fire extinguishers is a heavy metal tank filled with liquid carbon dioxide. When the valve on the tank is opened, the liquid carbon dioxide vaporizes. The vaporization, requiring heat, cools the issuing vapour and sublimates it to carbon dioxide "snow" that descends in a smothering cloud around the fire. An airport crash truck, equipped with these extinguishers, can discharge a ton of carbon dioxide on a burning plane in a few minutes. Liquid carbon dioxide can also extinguish fires in the motors of aeroplanes in flight. Another modern fire extinguisher effective on oil or gasoline fires makes use of sodium bicarbonate powder that has been treated to prevent caking. The powder is stored in heavy steel cylinders from which it is expelled on the fire by carbon dioxide gas liberated from a cartridge in the head of the cylinder. The powder, on becoming heated in the fire, liberates carbon dioxide and this smothers the flame. To extinguish small fires in ordinary combustible materials such as wood, paper, rubbish, etc.,

the soda-acid fire extinguisher (Fig. 17.10) is quite effective. The reaction between the sodium bicarbonate and sulphuric acid solutions, which mix when the extinguisher is tipped, produces large quantities of carbon dioxide. The resulting pressure not only causes some of the carbon dioxide to dissolve in the solution but also forces the liquid with considerable force through the nozzle. Both the cold water and the

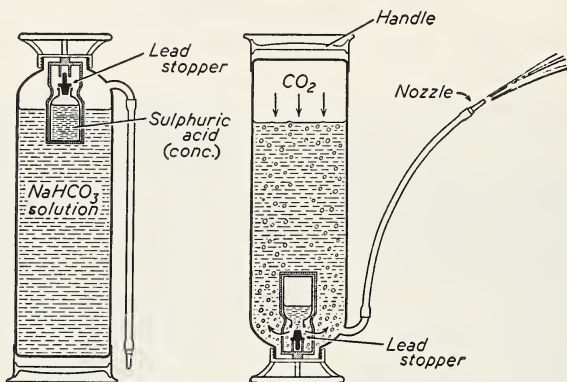
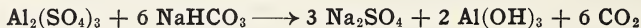


Fig. 17.10. The soda-acid fire extinguisher.

smothering effect of the carbon dioxide, liberated from the released liquid, are effective in extinguishing the fire:



Another fire extinguisher, efficient in extinguishing oil fires, contains licorice in the baking soda solution and concentrated alum solution in place of the sulphuric acid. The aluminum hydroxide produced by the reaction, together with the licorice, encloses the carbon dioxide in bubbles which form a persisting blanket of foam on the surface of the oil:



Because it is cheap and can be easily liquefied, carbon dioxide is employed to inflate rubber life preservers and rafts. A small metal cylindrical tank, a few inches long, contains enough carbon dioxide to inflate a small raft.

When carbon dioxide is "dissolved in water", some of the carbon dioxide reacts with the water to form carbonic acid, as previously stated, but most of the carbon dioxide actually dissolves, its molecules

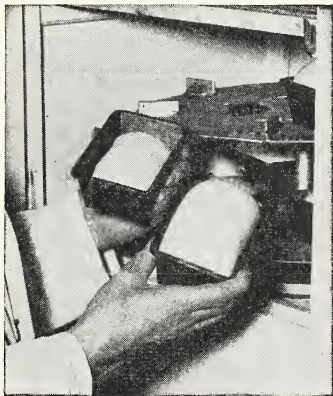
being dispersed among the molecules of water. For gases, similar to carbon dioxide which do not combine appreciably with water, it has been found that the weights of such gases, dissolving in a given volume of the solvent, are proportional to the pressure. This is known as **Henry's Law**.

At atmospheric pressure and 15°C ., one volume of water dissolves one volume of carbon dioxide. Thus, if the pressure is increased to 10 atmospheres, one volume of water will dissolve approximately 10 volumes of carbon dioxide. This is the principle utilized in the manufacture of soft drinks. Carbon dioxide is dissolved in sweetened, flavoured water under considerable pressure, bottled and capped. When the bottle is opened, the reduction in pressure causes most of the carbon dioxide to come out of solution. The escaping carbon dioxide bubbles, and the carbonic acid remaining, gives the beverage a pleasant, tangy taste.

Mention has been made (p. 174) of carbon dioxide "snow" and its usefulness in extinguishing fires. Solid carbon dioxide is made industrially in large quantities and is generally compressed into blocks and sold under the name of "dry ice". For purposes of refrigeration, this product, as its name implies, is dry, i.e. it vaporizes without going

through the intermediate liquid state. Vaporization requires heat, and the heat taken from the surrounding substances has a cooling effect on them. Ice cream trucks, restaurants, and companies dealing in quickly frozen foods use large quantities of "dry ice". This product is sometimes used in surgery to desensitize small areas of skin.

Another important use of carbon dioxide is in the **leavening** of the dough in bread, biscuits, and cakes. As carbon dioxide is produced within the dough, the bubbles formed give the mass a porous texture. Baking further increases the size of the enclosed bubbles as well as the porosity of the dough, and produces the chemical reactions necessary to change the dough into a digestible form. The greater area produced by the increased porosity results in the presentation of a greater surface of food to the digestive juices. For baking, carbon



C. I. L.

Fig. 17.11. Dough, leavened with yeast and ready for baking.

dioxide is commonly produced by one of three methods. In making bread, **yeast** plants are added to the dough and, as they grow, they cause fermentation of the sugar content thus producing carbon dioxide and alcohol. Baking drives off the alcohol in the form of vapour. For biscuits, sour milk and **baking soda** are used instead of yeast. The lactic acid in the sour milk reacts with the soda to liberate carbon dioxide. A third substance used in baking is **baking powder**. This is a mixture of baking soda, an acid-acting ingredient (such as cream of

tartar, tartaric acid, or sodium alum), and starch. Starch helps to keep the other ingredients dry and serves as a filler to give bulk to the powder and so make quantity measurements easy. When water is added to baking powder, the enveloping starch is washed off and the acid and carbonate react in solution to form carbon dioxide. The thousands of gas bubbles, trapped in the dough during the baking process, make the product "light".

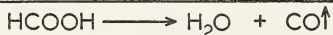
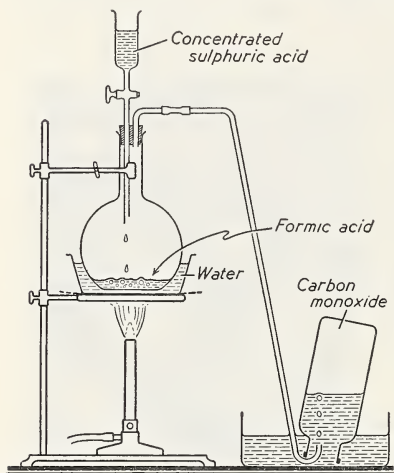


Fig. 17.12. The laboratory preparation and collection of carbon monoxide.

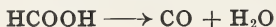
CARBON MONOXIDE

Occurrence. Carbon monoxide is produced whenever there is incomplete combustion as carbon fuels burn. Sometimes the gas escapes from defective furnaces. Although it is

not found in "normal" air, it is certain to be present in the exhaust gases from gasoline engines. Most manufactured gaseous fuels (Chapter 18) contain a high percentage of carbon monoxide.

Because carbon monoxide is intensely poisonous, its preparation and collection must be attempted only with extreme care.

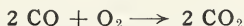
Preparation and collection. The most convenient laboratory preparation is by the action of concentrated sulphuric acid on formic acid (Fig. 17.12), or on sodium formate. The room should be well ventilated (open windows), and precautions taken to prevent the escape of more than small amounts of the gas into the room.



This reaction is an example of the dehydrating effect of concentrated sulphuric acid in its removal of hydrogen and oxygen, in the same proportion as they are found in water, from the decomposing formic acid.

Properties. Carbon monoxide is a colourless, odourless gas and is only slightly soluble in water. It is intensely poisonous and, if breathed continuously, one part in 1,500 parts of air will prove fatal. Its poisonous nature comes from its ability to combine with the haemoglobin of the blood to form a bright-red stable compound called **carboxy-haemoglobin**. Because the blood is no longer able to form **oxyhaemoglobin**, the oxygen-carrying pigment, the victim suffocates because of the lack of oxygen in his system. Symptoms of carbon monoxide poisoning are bright-pink lips and cheeks, and cherry-red blood. A person, overcome with carbon monoxide, should be taken into the open air and have artificial respiration applied. This should be followed by an inhalation of a mixture containing 93% oxygen and 7% carbon dioxide until there is a restoration of the normal rate of breathing.

Carbon monoxide burns with a blue flame to form carbon dioxide and nothing else. This is a simple test for the gas:



Carbon monoxide also has the ability to combine with the oxygen constituent of many metallic oxides.

Uses. Carbon monoxide is a powerful reducing agent and is necessary to the production of iron from iron ores:



Mixed with other gases, it is also burned as a fuel.



La France Fire Engine and Foamite

Fig. 17.13. An inhalator. The carbon dioxide administered with oxygen causes the diaphragm to contract thus initiating normal breathing.

OTHER COMPOUNDS OF CARBON

Carbon forms thousands of compounds with hydrogen. Any compound consisting of the two elements, carbon and hydrogen, is called a **hydrocarbon**. One of these hydrocarbons is acetylene (C_2H_2).

Acetylene. Preparation. Acetylene is usually prepared in the laboratory (in an impure form) by the action of water on calcium carbide

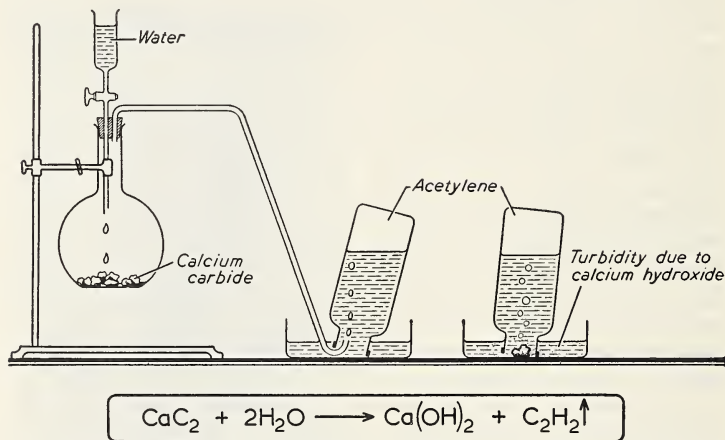
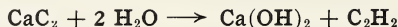
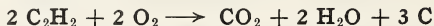


Fig. 17.14. The laboratory preparation and collection of acetylene. Two methods are shown.

(Fig. 17.14). If the acetylene is to be collected in pure form, it should be bubbled through acidified copper sulphate solution. It is collected over water as shown:

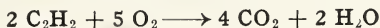


Properties. Pure acetylene is a colourless gas with a rather pleasant odour. It is soluble in its own volume of water and is very soluble in alcohol and acetone. Its density, compared with air, is 26 : 28.9. It is an unstable compound and, when compressed, is likely to explode with the evolution of much heat when it decomposes to form hydrogen and carbon. This renders the compression of the gas, and its storage under pressure, somewhat dangerous. Acetylene burns in air with a smoky flame (incomplete combustion):



When burned in burners of special construction (supplying sufficient

air for complete combustion) it gives a very brilliant flame. The products of complete combustion are carbon dioxide and water:



Two volumes of acetylene would require 5 volumes of oxygen (approximately 25 volumes of air) at S.T.P. for complete combustion.

A mixture of even one part of acetylene in 20 parts of air is explosive.

Uses. The main use of acetylene is in the oxy-acetylene torch, or blow-pipe (Fig. 17.16) for cutting and welding metals. The acetylene is stored under pressure in steel tanks containing felt or asbestos pads soaked in acetone. Acetone will dissolve many times its own volume of acetylene. When not more than 100 volumes are dissolved in acetone, it can be handled without danger. Fed with oxygen from an oxygen tank and ignited, a temperature of $3,500^\circ \text{C.}$ can be obtained. Such a flame will burn through heavy steel or armour plate. The flame, drawn slowly over the metal, melts it, and the excess oxygen used, burns the molten metal to its oxides that are blown off in a shower of sparks. For welding, the relative quantities of the two gases are adjusted so that the metal is melted but not oxidized. At the same time, a stick of the metal is melted by the blowpipe and the molten metal runs into the gap and is allowed to solidify to form a solid weld.

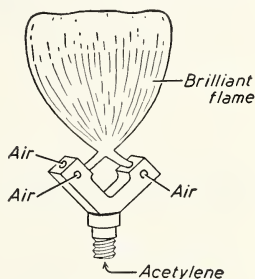


Fig. 17.15. A burner designed to supply sufficient air to burn acetylene for lighting purposes.

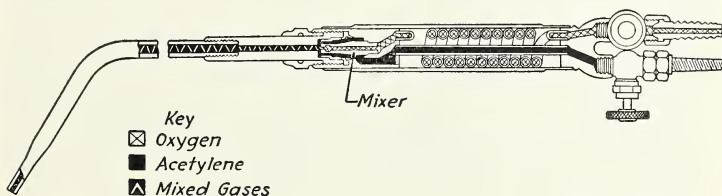


Fig. 17.16. Section of an oxy-acetylene torch.

The brilliancy of the flame produced when acetylene is burned with sufficient air makes it a suitable illuminating gas for use in isolated places.

Acetylene is also a starting point for the syntheses of many organic compounds including dyes, resins, synthetic rubber and acetic acid.

Carbohydrates. Carbohydrates are compounds containing carbon, hydrogen, and oxygen in which the proportion of hydrogen and oxygen is the same as in water. They include such substances as starch, cellulose, and various types of sugars. Starches and sugars are important food substances. They are the end-products of photosynthesis and the materials used by plants for food or for the manufacture of proteins and fats.

EXERCISE

A

1. Give an account of the occurrence of carbon both in the free and combined states. Distinguish clearly between varieties that are found in the mineral world and those that are not.

2. Give the properties of diamond and show how some of these properties have determined industrial uses for this form of carbon.

3. (a) Compare graphite with diamond. (b) Select those properties of graphite that make it useful in industry and give a use for each property selected.

4. What is meant by the term *amorphous*? What is the chief difference between amorphous and crystalline forms of carbon?

5. What are the five principal forms of amorphous carbon?

6. (a) Explain what is meant by destructive distillation? (b) Make a diagram of the apparatus used in the laboratory to illustrate the destructive distillation of wood. (c) Name the products of industrial value obtained from this process.

7. (a) How does wood charcoal differ from graphite? (b) Why does wood charcoal float on water?

8. Activated charcoal has great adsorbing properties. What is meant by this statement? How is charcoal activated and why does activation increase the adsorptive property?

9. How is boneblack manufactured? Describe how it is used in refining sugar.

10. Briefly describe the destructive distillation of coal and name the products formed.

11. Give five industrial uses of coke, and for each use state the property that determines it.

12. Distinguish between the channel and furnace methods of making carbon black. Why is carbon black pelletized?

13. List in order of importance the industrial uses of carbon black.

14. What is meant by *allotropic forms of carbon*?

15. How did Moissan prepare diamonds artificially?

16. How can it be proved that graphite is an allotrope of carbon?

17. Compare and contrast the two allotropes of oxygen.

18. What is the approximate percentage of carbon dioxide in the atmosphere? How is a balance of carbon dioxide in the atmosphere maintained?

19. Using a diagram to illustrate your answer, describe the laboratory method of preparing and collecting carbon dioxide. Write the equation for the reaction.

20. List the properties of carbon dioxide under (a) physical properties and (b) chemical properties.

21. Give five commercial uses of carbon dioxide and state the properties upon which each use depends.

22. (a) What are the effects of changes in pressure on the solubilities of gases? (b) Name and state the law that deals with pressure and the solubility of a gas.

23. Name three types of carbon dioxide fire extinguishers and explain the advantages of each.

24. (a) Explain why baking soda is not satisfactory for raising dough made with water or sweet milk. (b) If a cake recipe calls for sour milk, but you have only sweet milk, suggest how you could make the cake.

25. If a carbonated drink is allowed to stand uncorked in a warm place, its taste becomes flat. Explain, using an equation in your explanation.

26. Explain the action of yeast in the leavening of bread.

27. Using a diagram to illustrate your answer, describe the laboratory method of preparing and collecting carbon monoxide. Write the equation for the reaction.

28. (a) To what is the poisonous nature of carbon monoxide attributed? What are the symptoms of carbon monoxide poisoning and what is the method of treatment? (b) State the conditions that could cause a coal furnace to become a dangerous source of poisonous gas in the home.

29. Why is carbon monoxide a good reducing agent? Include an equation to illustrate your answer.

30. (a) Compare the two oxides of carbon in as many ways as you can. (b) State the Law of Multiple Proportions and illustrate it by reference to the two oxides of carbon.

31. Define a hydrocarbon and give an example.

32. (a) Using a diagram to illustrate your answer, describe the laboratory method of preparing and collecting acetylene. Write the equation for the reaction. (b) Why is the formula of acetylene C_2H_2 and not CH ?

33. (a) Write the equation for the complete combustion of acetylene. (b) In the combustion of acetylene explain why the percentage of carbon increases as the percentage of oxygen decreases. (c) State three commercial uses of acetylene.

34. Define *carbohydrate*. Give three examples of carbohydrates.

B

1. A sample of an organic compound was completely oxidized forming 5.3 gm. carbon dioxide. What weight of carbon was in the sample?

2. If 5 gm. coke on complete combustion gave 17 gm. carbon dioxide, find the percentage of carbon in the coke.

3. What weight of pure calcium carbonate is required to produce 22 gm. carbon dioxide using (a) hydrochloric acid; (b) sulphuric acid?

4. If 25 gm. marble containing 5% inert impurities react with excess hydrochloric acid, find the total weight of the products of the reaction.

5. From the formula of carbon dioxide, calculate its gram-molecular weight and its density compared with air (22.4 litres of air at S.T.P. weigh 28.9 grams).

6. Find the weight of a litre of carbon monoxide at S.T.P.

7. If 6.5 gm. acetylene are completely burned, calculate (a) the number of grams of oxygen required; (b) the volume of carbon dioxide produced if measured at S.T.P.; (c) the volume of water formed if measured at $4^\circ C$. and 760 mm. pressure.

8. (a) What volume of carbon monoxide measured at a temperature of $273^\circ C$. and a pressure of 1520 mm. of mercury will be oxidized by 80 gm. oxygen?

(b) How will the volume of carbon dioxide obtained in the above reaction com-

pare with the sum of the volumes of carbon monoxide and oxygen used, all being measured under the same conditions of temperature and pressure?

9. What weight of limestone, 75% pure, is necessary to produce 30 litres of carbon dioxide measured at 20° C. and 740 mm. pressure?

10. What volume of carbon dioxide measured at 15° C. and 749 mm. pressure will be necessary to convert 1 kilogram of sodium carbonate into sodium bicarbonate?

11. Calculate the density of carbon dioxide from the following data:

Weight of globe full of air at S.T.P. 949.7 gm.

Weight of globe exhausted 938.5 gm.

Weight of globe full of carbon dioxide at S.T.P. . . . 955.54 gm.

12. If 10 litres of carbon dioxide are passed over red-hot charcoal, what gas and what volume of this gas at S.T.P. will be formed?

13. A piece of limestone weighing 12.37 gm. was dropped into dilute sulphuric acid and left for three minutes. In that time 75 cc. of dry carbon dioxide at S.T.P. were collected. The piece of limestone was then removed, washed, dried, and weighed. What was its weight?

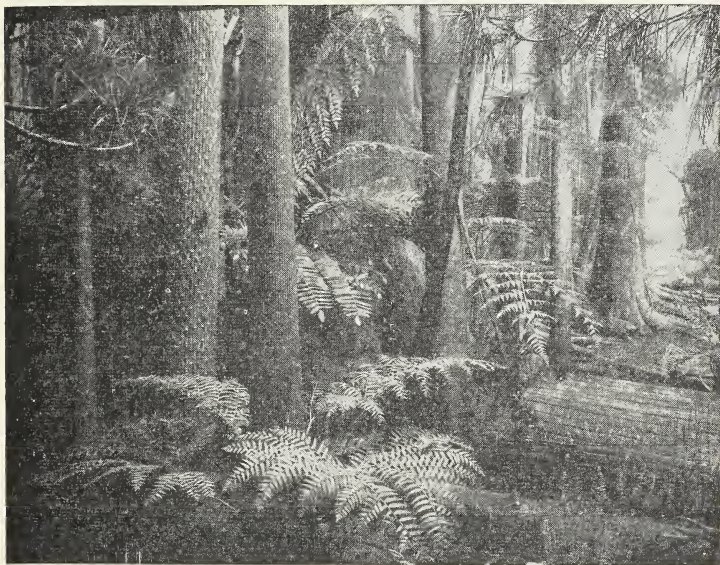
CHAPTER 18

Fuels and Flames

You now see the charcoal burning, but not as a flame, or if there be a flame, it is the smallest possible one which I know the cause of, namely the formation of a little carbonic oxide (carbon monoxide) close upon the surface of the carbon.

FARADAY

In the struggle for existence, man has become more and more aware of the importance of substances that are sources of chemical potential energy. All such substances may, in the general sense, be considered as fuels. Although great use is made of natural fuels, a number of artificial fuels have been manufactured, many of which are superior



Chicago Natural History Museum

Fig. 18.1. Photograph of a reconstructed forest in the Carboniferous Period, showing the luxuriant plant growth from which coal has formed.

to those produced by nature. Energy released by a fuel is the result of combustion and usually appears in the form of light or heat. Heat energy liberated by a fuel is measured in **British Thermal Units (B.T.U.)**. One B.T.U. is the amount of heat required to raise the temperature of one pound of water one Fahrenheit degree, and is equivalent to 252 calories. A high-grade anthracite coal produces approximately 15,000 B.T.U. per pound. From the point of view of the consumer, it would seem reasonable to purchase fuel according to its ability to liberate energy, but since many economic factors control market prices, this is not always possible.

There are three classes of fuels: solid, liquid, and gaseous. In the majority of these, carbon is the most important constituent.

SOLID FUELS

	B.T.U. Per Pound
Wood	8,000– 9,000
Bituminous coal	11,000–15,000
Anthracite coal	11,000–14,000
Coke	14,000

Wood. Wood, probably the first fuel used by man, was the only fuel employed for home heating a century ago, and it is still the chief fuel in remote wooded regions. The use of wood as a fuel is gradually diminishing because of its bulkiness, its relatively low heat content, and the necessity for forest conservation. The destructive distillation of wood (p. 168) produces wood alcohol and many other valuable products.

Coal. Coal is believed to have had its origin in the vast accumulations of the luxuriant plant growth of the Carboniferous Period. High temperatures and great pressures were factors which caused these organic deposits to be transformed into coal. The most important varieties of coal are anthracite (hard coal) and bituminous (soft coal). Anthracite may contain up to 90% free carbon. It burns with a clean blue flame and seldom gives off smoke. Bituminous contains less carbon but has much more volatile material. It shows layering, crumbles easily, and burns with a smoky flame. When bituminous coal is subjected to destructive distillation (p. 188), coke and other useful products result.

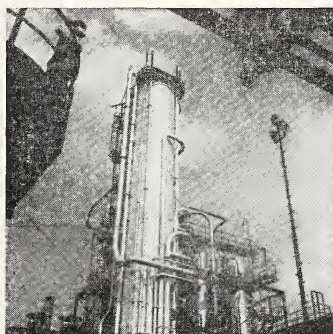
Coke. Coke, a porous mass of almost pure carbon, is equivalent to anthracite coal in heat value and burns with a smokeless flame. It is valuable as a domestic fuel and is indispensable in the production of iron from iron ores where it acts as a reducing agent.

LIQUID FUELS

	B.T.U. Per Pound
Alcohol (methyl)	11,620
Petroleum (crude oil)	19,500
Gasoline	20,750
Kerosene	19,810
Fuel Oil	18,500

Alcohols. The alcohols burn with a clean, hot flame and make excellent fuels, but they are rather limited in use because the cost of production makes them too expensive.

Petroleum. Petroleum (crude oil) is the greatest source of liquid fuels. It is a complex mixture of compounds containing carbon and hydrogen (hydrocarbons), and has a characteristic colour, odour, consistency, and composition, depending on the region from which it is obtained. Although the hydrocarbons in petroleum are principally liquids, many solid and gaseous hydrocarbons exist as solutes in solution. Petroleum can be used as a fuel in its natural state. However, through heating the petroleum and separately condensing the vapours of the various hydrocarbons, many purer products of greater value can be obtained. The process of refining petroleum in this way is known as fractional distillation, and the resulting products which volatilize between certain temperature limits may be classified into the following groups: naphtha, gasoline, kerosene, fuel oil, light lubricating oil, heavy lubricating oil, vaseline, paraffin, and petroleum coke.



Imperial Oil

Fig. 18.2. Crude oil, heated to 750°F., is pumped into this fractionating column or "bubble tower" at Imperial Oil's Sarnia Refinery. Primary separation is made into gases, gasoline, kerosene, gas oils, and reduced crude oil. These products are then piped to other units for further processing.

Fractional distillation is carried out in a fractionating column, or "bubble tower". The crude oil is heated in a large still connected to the fractionating column. The gases escape at the top; the lightest fractions (lowest boiling points) enter special tubes near the top of the tower and condense, and the heavier fractions (higher boiling points) condense, each at its own particular level. **Gasoline** is the most important fraction. Because of the increasing demand for gasoline, chemists

have invented "cracking" processes that break the heavier hydrocarbon molecules into lighter "gasoline" molecules. Along with the necessity for more gasoline came the need for better gasoline. Much research has gone into the production of anti-knock compounds, anti-oxidants, and high "octane ratings". With automobile companies manufacturing more efficient internal combustion engines with increased cylinder compression ratios and decreased engine weight, the refineries have been forced to provide more efficient fuels.

In its various grades, **fuel oil** occupies an important place in modern living. Diesel engines operate on this relatively cheap fuel as do oil-burners used for domestic heating. **Kerosene**, formerly used extensively in oil lamps, is now being largely converted into gasoline.

GASEOUS FUELS

	B.T.U. Per Cu. Ft.
Natural gas (variable composition)	1,000-2,000
Coal gas (variable composition)	appr. 600
Water gas	appr. 300
Carburetted water gas	appr. 550
Producer gas	appr. 130
Acetylene	appr. 450

Natural gas. The term "natural" distinguishes the gases found trapped in pockets of the earth from "artificial" gases. Natural gas, being a mixture, has a variable composition. Its main component is either methane (CH_4) or ethane (C_2H_6). It was first discovered in Ontario in 1891 and piped to Detroit and Buffalo for industrial use. The most important source, to date, in Canada is the Viking-Kinsella Field in Alberta. Natural gas is generally associated with petroleum on which it creates a pressure sufficient to force the petroleum to the surface. Most Canadian natural gases contain a small percentage of helium. Carbon black results when natural gases burn in a limited supply of air.

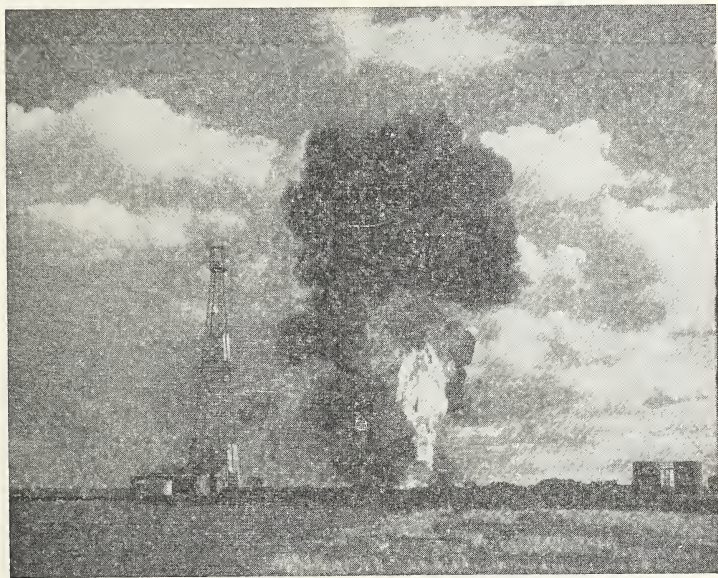
Where natural gas is not available, artificial gases are manufactured for industrial and domestic purposes.

Coal gas. The destructive distillation of bituminous coal produces combustible gases (appr. 12,000 cu. ft. per ton) composed mainly of methane and hydrogen and possibly some carbon monoxide. Impurities are removed by passing the hot gases through a series of condensers and scrubbers to remove coal tar, ammonia, and sulphur compounds. The purified gas is stored under pressure in gas holders from which it is distributed to the consumers.

Water gas. The following equation represents the chemical reaction taking place when water gas is produced.



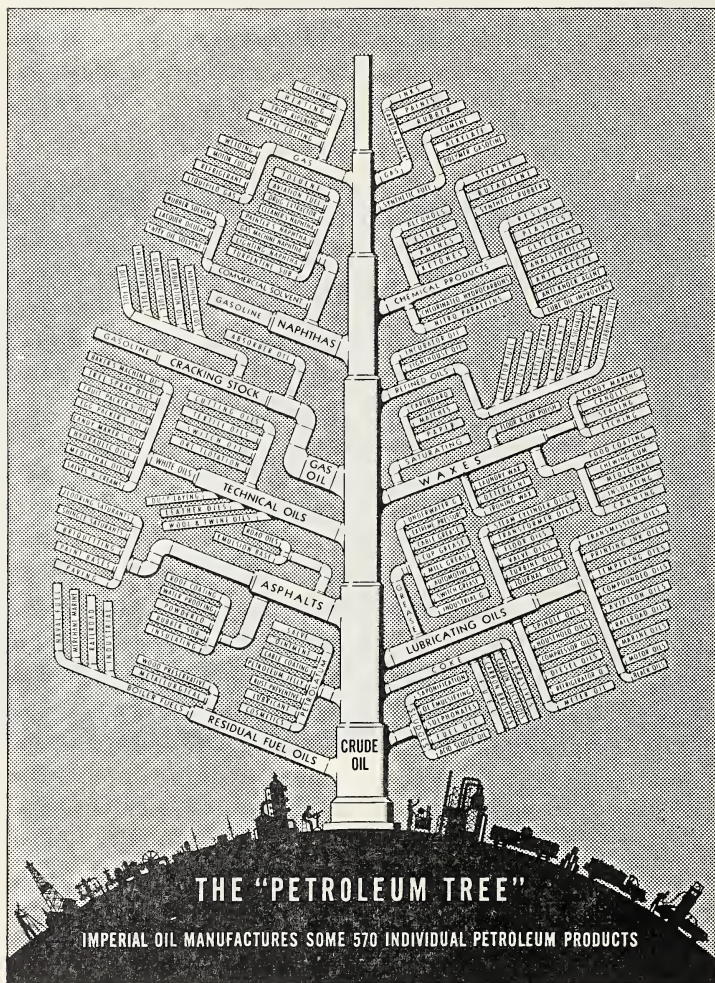
Steam is passed through a mass of coke heated to a white heat. Since the reaction is endothermic, the temperature of the coke falls rapidly and it is necessary to turn off the steam intermittently and admit a blast of air. This causes the coke to burn and raises the



Imperial Oil

Fig. 18.3. Imperial Leduc #3 blowing into production. The first flow is burned in a flare because it is contaminated with mud, water, and chemicals used in drilling the well. When the well is cleaned out, the oil is turned into the storage tanks.

temperature of the coke again to a white heat. Water gas, so produced, is more valuable for heating than lighting since the two gases, carbon monoxide and hydrogen, burn with little light. Water gas is also a valuable source of hydrogen used in the synthesis of ammonia and in the hydrogenation of oils. By controlling the quantity of air, and through the use of suitable catalysts, the carbon monoxide may be converted to carbon dioxide and separated from the hydrogen. To make water gas valuable as an illuminant, a petroleum oil is vaporized



Imperial Oil

Fig. 18.4. The many products that result from crude oil.

in a special container where it is "cracked" into lighter hydrocarbons, and these are added to the water gas. Hydrocarbons in the water gas increase the illuminating power of the flame. After this treatment water gas is called **carburetted water gas**.

AVERAGE YIELD FROM A BARREL OF RAW MATERIAL SUPPLIED

1949		1950
42.0%	← GASOLINES →	40.2%
23.8%	← DISTILLATE FUELS →	25.8%
19.6%	← HEAVY FUEL AND GAS →	20.2%
6.9%	← OTHER PRODUCTS →	6.4%
7.7%	← CONSUMED IN OPERATIONS →	7.4%

GASOLINES INCLUDE AVIATION AND MOTOR FUELS, TRACTOR DISTILLATES, NAPHTHA SPECIALTIES, SOLVENTS, ETC. • DISTILLATE FUELS INCLUDE KEROSENE, STOVE OIL, FURNACE FUEL OIL, DIESEL FUEL AND INDUSTRIAL GAS OILS • OTHER PRODUCTS INCLUDE LUBRICATING OILS, GREASES, ASPHALTS, COKES, WAXES, ETC.

Imperial Oil

Fig. 18.5. Relative amounts of products obtained from crude oil.

Producer gas. Producer gas is a cheap industrial fuel easily manufactured from low-grade coal. An air blast containing some steam is forced through a thick bed of coal heated to a high temperature. The carbon dioxide produced by oxidation is reduced to carbon monoxide in the upper layers of incandescent carbon. This carbon monoxide mixes with the water gas resulting from the action of the steam on the hot coal. These combustible gases are diluted with relatively large amounts of nitrogen which reduce the fuel value of producer gas.

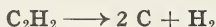
Acetylene gas. Acetylene as a fuel finds its greatest value in the oxy-acetylene torch for welding and cutting metals.

FLAMES

It has been previously stated that the energy released by a fuel is the result of combustion, and appears in the form of light or heat. Burning with a "flame" differs from burning with a "glow" in that a flame always indicates a chemical reaction between gases, whereas a glow indicates oxidation without the formation of a gaseous state.

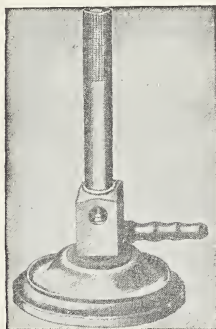
Burning solids do not emit a flame unless volatile matter is expelled, hence iron burns in oxygen without a flame, and unless carbon monoxide is formed, carbon burns without a flame.

The luminosity of a flame is generally caused by the presence of glowing solid matter such as incandescent carbon or quicklime. Acetylene, for example, is a hydrocarbon that decomposes when heated:



The luminosity is produced by the free carbon. Complete and incomplete combustion of acetylene are discussed in Chapter 17.

In order to obtain the most heat from a fuel it is necessary to insure its complete combustion. The equation, $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2 + 94,390$ cal., represents the complete combustion of 12 gm. of carbon, whereas the equation $2 \text{C} + \text{O}_2 \longrightarrow 2 \text{CO} + 26,430$ cal. shows the incomplete combustion of the same weight of carbon. It is quite evident that the incomplete combustion of a fuel results in a drastic reduction in the heat value.



Fisher Scientific Company

Fig. 18.6. The original Bunsen burner.

The admission of air to the mixing chamber of a **Bunsen burner** is controlled by a special valve or collar near the base of the barrel. When the air inlet is completely closed, the surrounding flame produces only enough heat to burn the hydrogen set free by the decomposition of the hydrocarbons. The carbon set free is in the form of fine particles that become incandescent and produce the characteristic yellow-coloured flame. As soon as more air is allowed to enter, the flame becomes almost invisible because of the complete combustion of the carbon particles. If still more air is admitted, the flame takes on the appearance of two cones, a pale-blue outer cone (complete combustion) and a smaller greenish cone (incomplete combustion). An excess of air cools the middle zone and so prevents the decomposition of some of the hydrocarbons. Sometimes, if the gas is gradually turned off, a point is reached where the proportion of air becomes so great that the gas mixture explodes and "strikes back" setting the gas burning at the jet.

In a **candle flame** the melted hydrocarbons in the paraffin are led by capillary action to the tip of the wick where they are converted

into a vapour. This vapour burns in the insufficient supply of oxygen brought in by the convection currents and produces the characteristic yellow sooty flame.

Incomplete combustion of fuels causes great losses in industry and many attempts have been made, and are being made, to reduce the waste. Forced drafts, powdered fuels, and careful adjustments of oil-

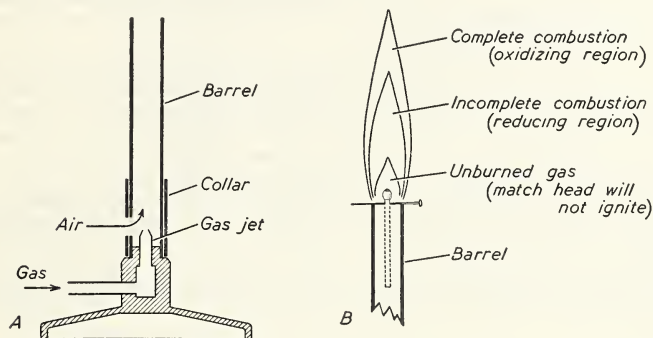


Fig. 18.7. A, Bunsen burner in section. B, diagram showing the various regions in a Bunsen flame.

burner jets and carburetors in internal combustion engines, all tend to promote complete combustion by means of which money is saved for the consumer and the potential energy resources of the nation are conserved.

FLAME TEMPERATURES

Type of Flame	Highest Temperature
Bunsen (coal gas)	1570° C.
Meker (coal gas)	1871° C.
Blowpipe (coal gas)	2200° C.
Oxy-hydrogen blowpipe	2800° C.
Oxy-acetylene blowpipe	3500° C.
Hydrogen (atomic)	4200° C.

EXERCISE

A

1. (a) What property is common to all fuels? (b) Why is electricity not considered a fuel? (c) What factors should be considered in determining the kind of fuel to be used in the home?

2. (a) Name four solid fuels. (b) Give three reasons why the use of wood as a fuel is diminishing. (c) Compare anthracite and bituminous coals with respect to (i) formation; (ii) carbon content; (iii) structure; (iv) burning properties.

3. (a) Name five liquid fuels. (b) Which of these fuels gives the most heat on complete combustion?

4. (a) What is meant by fractional distillation? (b) Describe a fractionating column and explain how it separates the components of crude oil. (c) Name ten products resulting from the fractional distillation of petroleum.

5. (a) Name six gaseous fuels. (b) Of the gaseous fuels named state which has the greatest heat value and which the least. (c) Compare coal gas, water gas, producer gas and acetylene with respect to (i) method of preparation; (ii) composition; (iii) cost of production; (iv) use.

6. (a) How does burning with a *flame* differ from burning with a *glow*? (b) Coal gas burns with a luminous flame. Hydrogen burns with a non-luminous flame. Account for this difference.

7. (a) With the aid of a diagram describe the construction of a Bunsen burner. (b) Under what condition does the Bunsen burner give (i) a luminous flame and (ii) a non-luminous flame? (c) What precautions should be taken to keep the burner from "striking back"? (d) Give two reasons why a Bunsen burner that has struck back should promptly be turned off.

8. Describe the structure and composition of a candle flame.

9. What is the difference between complete and incomplete combustion? Which is usually more desirable? Why? Write equations to illustrate your answer.

10. When smoke is seen coming from the chimney of an industrial plant it is an indication of inefficiency. Explain what remedial measures would improve the situation.

B

1. The reaction that takes place when steam is passed over white-hot coke to form water gas may be represented by the equation: $C + H_2O \longrightarrow CO + H_2$. (a) Assuming that the coke is 90% carbon and that 100 kilograms of coke are used, calculate the number of litres of water gas, measured at 273° C. and 950 mm. pressure, that would be produced. (b) What proportion by volume of the resulting water gas is carbon monoxide?

2. How many litres of oxygen would be required for the complete combustion of 10 litres of water gas, all gases measured at the same temperature and pressure?

CHAPTER 19

Sulphur and Its Compounds

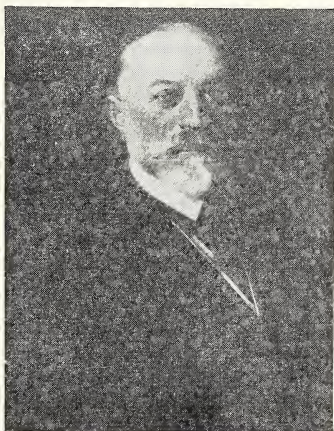
And evermore, wher ever that they gon,
Men may them knowe by smellyng of bremstoon;
For al the world they stynken as a goat,
Their savour is so rammysh and so hot,
That though a man from them a myle be,
The savour will infect him, truste me.

CHAUCER

Sulphur has for centuries excited great interest in the minds of students of alchemy and chemistry. Possibly, because sulphur may be burned away without leaving any ashes, an impression was obtained that it was a principle of fire and existed in all combustible bodies. The foul odour of some of the compounds of sulphur, or brimstone as the alchemists knew it, led Leo Africanus (about 1500 A.D.) to write that "chemists are a most stupid set of men who contaminate themselves with sulphur and other horrible stinks". Chaucer, a century earlier, had much the same idea.

SULPHUR

Occurrence. Sulphur resembles oxygen in that it occurs in nature both in the free state and in combination with other elements. In its combined state, sulphur is usually associated with metals, and the minerals are valued more for their metal than for their sulphur content. Most of these minerals are either **sulphides** or **sulphates**. The sulphides include pyrites (FeS_2), chalcopyrites (CuFeS_2), cinnabar (HgS), galena (PbS), and sphalerite or zinc blende (ZnS). Sulphides of silver, tin, nickel, arsenic, and antimony also occur in nature. The sulphates include gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$), Epsom



Freeport Sulphur Co.

Fig. 19.1. Herman Frasch (1852-1914), an American chemist, invented the modern method of obtaining sulphur.

salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and barytes (BaSO_4).

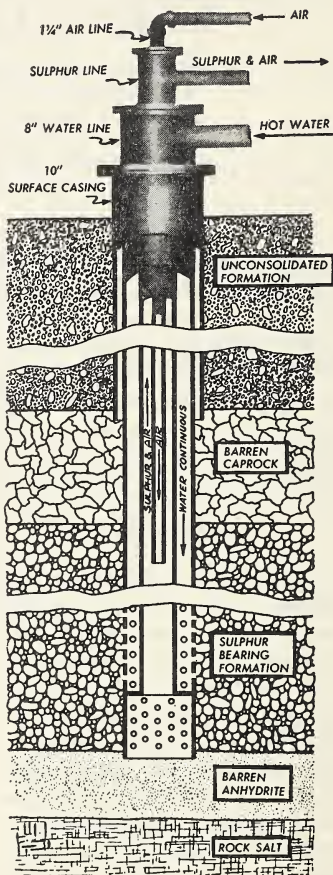
Sulphur is also present in many animal and plant substances such as eggs, onions, and meat.

Extraction. Most of the sulphur used in industry is mined from native sulphur. Prior to 1903, much of this came from Sicily where it is found free but mixed with volcanic rocks. The rock mass is heated by burning sulphur. In the process, the unburned sulphur melts and is run off and purified by distillation. If the vapours are suddenly cooled, **flowers of sulphur** sublime; if the vapours cool slowly, liquid sulphur is formed and is run into molds to give **roll sulphur**. Sulphur, found in the dormant volcano Popocatepetl in Mexico, is treated in much the same manner as in Sicily.

More than three-fourths of the world's supply of sulphur is now produced in the United States. In 1867, while drilling for oil in Louisiana, geologists found a sulphur deposit at a depth of about 500 feet buried beneath layers of bog, quicksand, and rock. Because of the quicksand and the poisonous hydrogen sulphide fumes permeating it, efforts to sink a shaft to mine the sulphur ended in disaster.

By connecting the two facts that the melting point of sulphur is 112.8°C . and that the boiling point of water can be raised by increasing the pressure, a young chemist, Herman Frasch, perfected the modern sulphur mining method.

This method is now used extensively in Texas and Louisiana where there are many deposits similar to those of the original discovery.



Freeport Sulphur Company

Fig. 19.2. The piping system used in the Frasch method of obtaining sulphur.

A typical sulphur deposit is somewhat egg-shaped, about half a mile in diameter and almost 500 feet thick.

In the **Frasch process**, a well is drilled and a 10-inch pipe driven to the top of the sulphur deposit. This pipe serves as a casing for three concentric pipes within, an 8-inch "hot water pipe", a 3-inch "sulphur pipe", and a $1\frac{1}{4}$ -inch "compressed air pipe". The 8-inch pipe is perforated at the lower end and extends to the bottom of the sulphur deposit. Water, superheated to a temperature of about 170°C . and under a pressure of about 120 pounds to the square inch, is forced down this pipe and hot compressed air is forced down the $1\frac{1}{4}$ -inch pipe. The combined water and air pressures force the melted "air-filled" sulphur, in the form of frothy foam, up the 3-inch pipe. The molten sulphur is directed towards storage bins, one of which will hold many thousands of tons, and allowed to solidify into mountainous-sized blocks. From the solid mass, sulphur is blasted and scooped into railway cars. Sulphur obtained by the Frasch process is more than 99.5% pure and several million tons are produced annually. When Frasch first suggested "pumping a solid out of the earth", there was a scoffer who offered to "eat every ounce of sulphur pumped". What a time he would have had making good his offer!

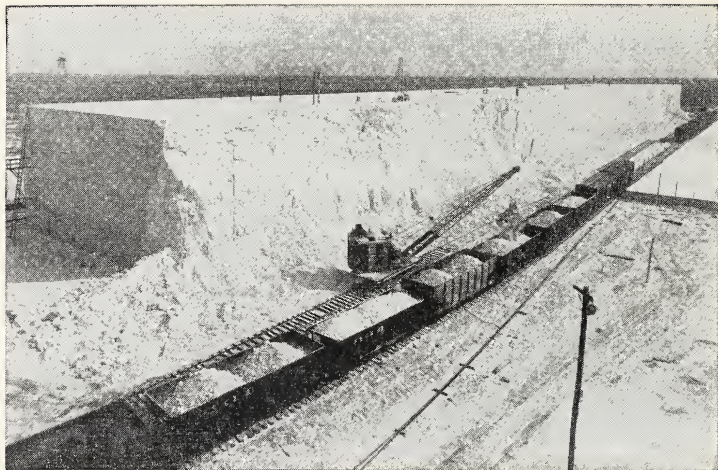
The recent discovery of a sulphur bed in north central Alberta may result in Canada's first Frasch-process plant for sulphur production.

Physical properties. Sulphur exists in three different forms, rhombic, prismatic, and amorphous. These allotropic modifications have different shapes, colours, densities, and solubilities, but their chemical behaviour is the same. **Rhombic sulphur** is the stable form at ordinary temperatures and comprises almost all the sulphur used in commerce. It is a pale-yellow, brittle, crystalline, odourless, tasteless solid. The crystals are rhombic, or octahedral, in shape. Rhombic sulphur is insoluble in water but readily soluble in carbon disulphide. It has a specific gravity of 2.06 and melts at 112.8°C . Large crystals of this form may be prepared by dissolving roll sulphur in carbon disulphide and allowing the solvent to evaporate slowly.



Freeport Sulphur Company

Fig. 19.3. Molten sulphur emerging from underground and flowing into a bin.



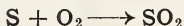
Texas Gulf Sulphur Company

Fig. 19.4. A huge pile containing many hundreds of tons of solidified sulphur. The sulphur is loaded into open cars by a power shovel.

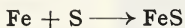
Prismatic, or monoclinic, sulphur is stable only between 96°C . and 119°C . It, too, is crystalline, but the crystals are needle-shaped and transparent and have a specific gravity of 1.96. It is insoluble in both water and carbon disulphide, but because it changes to rhombic sulphur below 96°C ., when allowed to stand in cold carbon disulphide for some time it will disappear. It is prepared by cooling melted sulphur to the point where it solidifies on the surface, then breaking the crust and pouring off some of the molten interior. Long needle-like monoclinic crystals will fill the container.

If sulphur is carefully melted, it first forms a thin, straw-coloured liquid. As the temperature rises, the liquid thickens and darkens in colour until, at about 200°C ., the viscosity is so high the sulphur will not run out of an inverted dish. At this temperature it is reddish-brown in colour. As the temperature rises, the sulphur becomes thin again and, at 445°C ., it boils. If the boiling sulphur is suddenly cooled by pouring it into cold water, it forms a gummy, elastic solid, varying in colour from amber to dark brown. This **plastic, or amorphous, sulphur** is tough and elastic and is not soluble in either water or carbon disulphide. It changes to the rhombic form on standing.

Chemical properties. Sulphur burns in air with a pale-blue flame:



When heated, it becomes very active, uniting directly with most metals to form sulphides. For example, when a mixture of iron filings and sulphur is heated, the mass glows brightly even after it has been removed from the flame producing ferrous sulphide:



It also unites, but less vigorously, with some non-metals.

The compounds formed by sulphur are analagous to the corresponding oxygen compounds.

<i>Oxides</i>	<i>Sulphides</i>
H ₂ O	H ₂ S
CO ₂	CS ₂
FeO	FeS
CuO	CuS
ZnO	ZnS
MgO	MgS

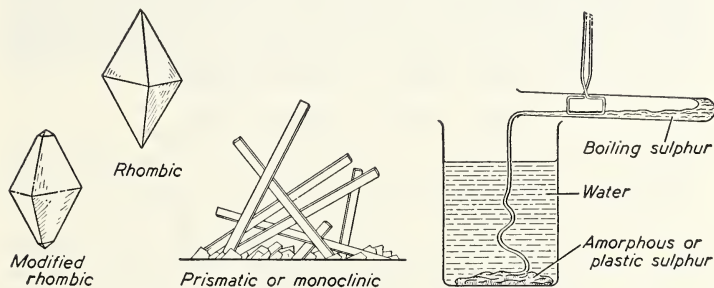


Fig. 19.5. The allotropic forms of sulphur.

Uses. About half of the sulphur mined is used in the manufacture of sulphuric acid, probably the world's most important chemical compound. Large quantities of sulphur are also used in **vulcanizing** rubber, during which process rubber is made tough, hard, and durable. Vulcanization, discovered accidentally in 1839 by Charles Goodyear, consists of heating melted sulphur and rubber.

Additional uses of sulphur occur in the manufacture of calcium bisulphite, $\text{Ca}(\text{HSO}_3)_2$, a bleaching agent used in making wood pulp; gunpowder; matches; fireworks; dyes; medicine; fumigation; and



Goodyear Tire and Rubber

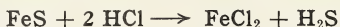
Fig. 19.6. Charles Goodyear (1800-1860) discovers how to vulcanize rubber. A mixture of rubber and sulphur was accidentally dropped on a hot stove. Prior to this time rubber was sticky and gummy in hot weather and hard and brittle in cold weather. Vulcanized rubber is plastic and is not affected by temperature changes.

ointments for the treatment of skin diseases. Lime-sulphur spray, made by boiling together sulphur, water and slaked lime, is helpful in checking fungous diseases of plants.

HYDROGEN SULPHIDE (H_2S)

Occurrence. Hydrogen sulphide is found in nature wherever putrefaction of animal or vegetable matter occurs. It is also found among vapours issuing from volcanoes, and in some natural gases. Solutions of hydrogen sulphide occur as natural waters called "sulphur springs".

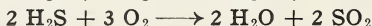
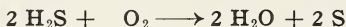
Preparation. The convenient laboratory method of preparation is by the action of dilute hydrochloric acid on a metallic sulphide. The sulphide most commonly used is ferrous sulphide.



The gas is collected by the upward displacement of air (Fig. 19.7).

Properties. *Physical.* Hydrogen sulphide is a colourless gas with an offensive odour like that of rotten eggs. The putrefaction of any organic matter containing sulphur results in this same offensive odour. It is slightly denser than air (34:28.9), fairly soluble in water, and can be easily liquefied. It is a very poisonous gas, but fortunately its odour gives due warning of its presence.

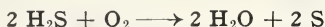
Chemical. Hydrogen sulphide is somewhat unstable. If heated out of contact with air, it will decompose to form sulphur and hydrogen. In air, it burns with a pale-blue flame to form water, and either sulphur or sulphur dioxide depending on the proportion of air supplied.



A mixture of two volumes of hydrogen sulphide and three volumes of oxygen explodes on ignition (complete combustion). If moist hydrogen sulphide and sulphur dioxide are mixed, the sulphur dioxide is reduced.



If a solution of hydrogen sulphide is allowed to stand, it is oxidized by the dissolved oxygen in the water and white sulphur precipitates.

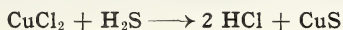


A solution of hydrogen sulphide is a very weak acid and is known as **hydrosulphuric acid**. Salts of this acid are called **sulphides**.

A piece of paper that has been dipped into lead acetate solution turns brown and then black when exposed to hydrogen sulphide. This is the characteristic **test** for the gas.

Uses. The only important use of hydrogen sulphide is in chemical analyses. Because of the instability of hydrosulphuric acid, a Kipp generator is usually used in the laboratory for the preparation of the gas as needed.

Most of the metallic sulphides are insoluble in water and some of them are insoluble in acids. In addition, sulphides show a variety of quite distinctive colours. Because of these characteristics, a chemist can use hydrogen sulphide to detect the presence of metal ions in solution. For example, if hydrogen sulphide is bubbled into a dilute acid solution containing cupric chloride, a black precipitate of cupric sulphide results.



If hydrogen sulphide is bubbled into an acid solution of zinc chloride,

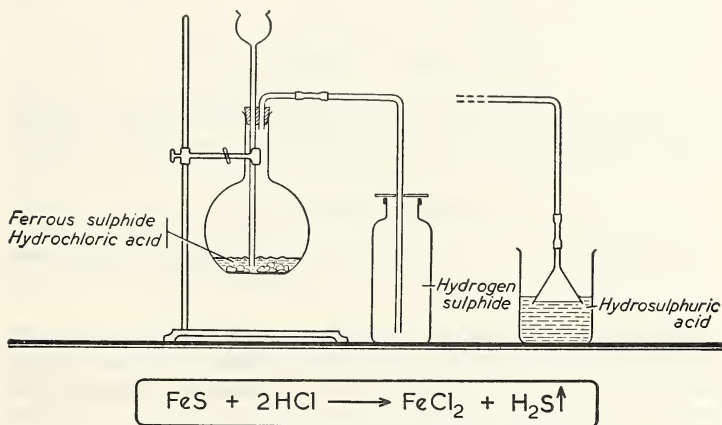


Fig. 19.7. The laboratory preparation and collection of hydrogen sulphide.



Canadian Industries Limited

Fig. 19.8. Using a helicopter to dust with lime-sulphur.

no precipitate is formed, but if the solution is only slightly acidic, a white precipitate of zinc sulphide results.

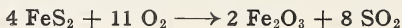


By applying a knowledge of colours and solubilities under certain fixed conditions, the chemist can determine the presence or absence of many of the metal ions in a solution.

SULPHUR DIOXIDE (SO_2)

Occurrence. Sulphur dioxide is found in gases issuing from volcanoes. Traces are also found in the air of industrial towns where coal, containing sulphides, is burned.

Preparation. Industrially, large quantities of sulphur dioxide are prepared by burning sulphur in air or by **roasting** a metallic sulphide, generally pyrites (FeS_2). Roasting consists of heating in contact with air.



Sulphur dioxide can also be produced by heating copper and concentrated sulphuric acid. The most convenient and common laboratory method of preparation consists in dropping sulphuric acid into a concentrated solution of sodium bisulphite and collecting the gas by the upward displacement of air (Fig. 19.9).

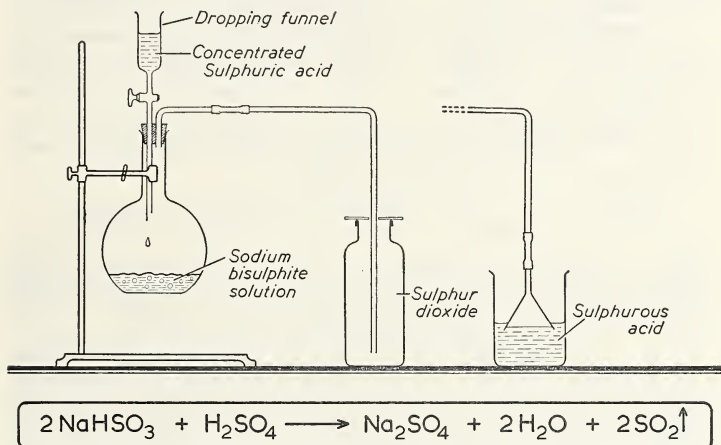
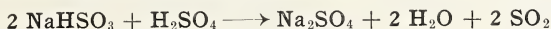
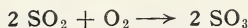


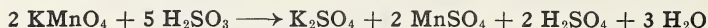
Fig. 19.9. The laboratory preparation and collection of sulphur dioxide.

Properties. Physical. Sulphur dioxide is a colourless, poisonous gas with a penetrating, suffocating odour. In the preparation of the gas, there often appears a whitish cloud caused by minute quantities of sulphur trioxide. Sulphur dioxide is very soluble in water, one volume of water dissolving 80 volumes of the gas at S.T.P. It is 2.2 times as dense as air and can be easily liquefied at ordinary temperatures. **Chemical.** Sulphur dioxide does not burn nor does it support combustion. It acts as a reducing agent, in the presence of a catalyst, to form sulphur trioxide.



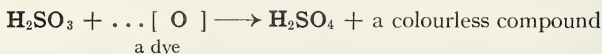
When it is said that sulphur dioxide is "soluble", what is meant is that it *reacts* with water to form sulphurous acid (H_2SO_3) solution that has all the characteristics of an acid. However, the compound, H_2SO_3 , has not been isolated because heating drives off sulphur dioxide. In this respect, sulphur dioxide resembles carbon dioxide. It acts as an

oxidizing agent with hydrogen sulphide. It reduces a solution of potassium permanganate, thereby changing it from a purple to a colourless solution. This serves as a characteristic test.



Uses. 1. *As a refrigerant.* Because of the ease with which it can be liquefied, and because of its relatively high heat of vaporization (95 calories), sulphur dioxide is sometimes used as a refrigerant.

2. *In bleaching.* Sulphur dioxide reacts with some coloured substances to form colourless compounds. The bleaching is brought about by a reducing action in which the sulphur dioxide robs the colouring matter of part of its oxygen to produce a colourless compound. The reactions with organic dyes are quite complex, but could be represented by the following equation.

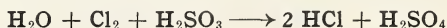


Sulphur dioxide is used to bleach wool, silk, and straw, to all of which chlorine would be injurious. Substances bleached by sulphur dioxide often return to their original colour because of reoxidation.

3. *As a food preservative.* Dried fruits, treated with sulphur dioxide, will keep longer because all bacteria present will be killed. Corn syrup, bleached with the gas, and Maraschino cherries, bleached and then artificially coloured, do not easily mould or decay. Excessive quantities of sulphurous acid, however, are likely to be injurious to health.

4. *In making sulphites.* Wood chips are both bleached and converted to pulp by cooking in a calcium bisulphite solution made by the action of sulphur dioxide on slaked lime.

5. *For dechlorinating water.* Great quantities of sulphur dioxide are used to improve the taste of water supplied to large cities, e.g. Toronto. In addition to killing bacteria, chlorine in excessive doses (super-chlorination) will partially remove from water any objectionable taste caused by refuse from industrial plants, but it does leave the water with a strong chlorinous flavour. Sulphur dioxide is then used to react with the excess chlorine to form hydrochloric and sulphuric acids in the removal of the objectionable taste.



Both acids are removed by a reaction with the bicarbonates commonly found in hard water to form chlorides and sulphates. A more recent method employed to improve the taste of water, and one not requiring dechlorination, makes use of chlorine dioxide (ClO_2).

6. *In making sulphuric acid.*

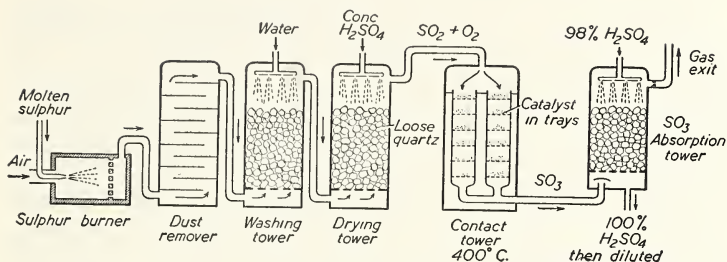


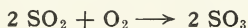
Fig. 19.10. The contact method for making sulphuric acid.

SULPHURIC ACID (H_2SO_4)

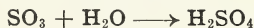
Preparation. Sulphur trioxide is the anhydride of sulphuric acid. Therefore the problem of finding a commercial method of preparing this acid resolves itself into the problem of making sulphur trioxide in quantity. This was solved with the discovery of a suitable catalyst that hastened the oxidation of sulphur dioxide.

Contact process. The catalyst first used was platinum, prepared by heating asbestos fibres, previously soaked in chloroplatinic acid, and heating the asbestos until the acid decomposed to form finely divided platinum on the fibres. The sulphur dioxide can be formed by burning (roasting) iron pyrites (FeS_2) or by burning pure sulphur. Arsenic impurities usually present in the pyrites “poison” the platinum so that it loses its catalytic properties. Today, in the most modern plants, vanadium pentoxide, deposited on a preparation of silica, is being increasingly used. It is unaffected by arsenic impurities and is just as efficient a catalyst as platinum.

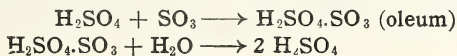
Sulphur dioxide and air, at a temperature of about $400^\circ\text{C}.$, are passed over the catalyst and sulphur trioxide results.



The sulphur trioxide with water gives sulphuric acid.



Actually in industry a better recovery is effected by “dissolving” the sulphur trioxide in previously prepared sulphuric acid and then diluting to give the grade of acid required by the trade.

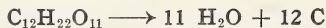


Chamber process. This method uses nitrogen dioxide as the catalyst, and the reaction occurs in the presence of steam or a spray of water in large lead chambers. The reaction takes place slowly and therefore the gases are allowed prolonged contact (about three hours) with one another in the lead chambers. The nitrogen dioxide is recovered for use again. The acid produced is known as chamber acid and is never more than 70% sulphuric acid, but it can be further treated to concentrate and purify it. Chamber acid is used in processes not requiring a pure product, e.g. the manufacture of washing soda, ammonium sulphate, superphosphate of lime, etc. The contact acid is used in the preparation of certain food stuffs, dyes, drugs, and batteries.

Properties. *Physical.* Pure sulphuric acid is an oily liquid which can be frozen to form white crystals. Pure acid is seldom made, and it can be prepared only with difficulty. Dilute acid can be concentrated only to 98.3% by boiling. This concentrated acid, commonly called "oil of vitriol", is also oily in appearance, has a specific gravity of 1.84, and boils at a very high temperature of 338° C. It is colourless, but commercial acid may be brown or black depending on the presence of organic impurities. The pure acid is a non-electrolyte, but it conducts electricity readily when it is diluted.

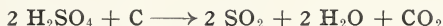
Chemical. Concentrated sulphuric acid has a great affinity for water. When the acid is added to water, a great deal of heat is evolved; thus the acid should be added in a thin stream with constant stirring so that the large volume of water may absorb the heat developed. *Water should never be poured into the concentrated acid* because "local" heating will cause boiling and scatter the acid. The action with water is chemical and exothermic and forms a liquid hydrate of sulphuric acid ($\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$).

The attraction of concentrated sulphuric acid for water is so great that it will decompose a large number of substances containing hydrogen and oxygen in the same proportion as they are found in water eliminating these elements from the compound as water, with which the acid combines (dehydrating action). Thus cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), starch, cotton, and wool, all of which contain carbon, oxygen, and hydrogen become **carbonized** when concentrated sulphuric acid is added. At the same time, hydrogen and oxygen are removed as water, leaving a black porous mass of carbon:

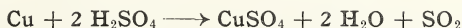


Hot concentrated sulphuric acid acts as an oxidizing agent, and during oxidation is itself reduced by many substances to either sulphur

dioxide or sulphur. If charcoal is boiled in the acid, the carbon is oxidized to carbon dioxide:



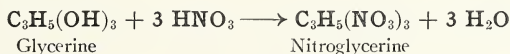
The action of sulphuric acid on metals depends upon the concentration and temperature of the acid as well as on the nature of the metal involved. Thus dilute acid reacts with most metals with the formation of sulphates and hydrogen. However, it does not affect mercury, copper, gold, silver, or platinum. Aluminum reacts slowly with dilute acid but if the acid is warmed the action is vigorous, and hydrogen and aluminum sulphate are formed. Cold concentrated acid has practically no effect on the metals (except sodium, potassium, and magnesium). The hot concentrated acid, however, acts on most metals to form sulphur dioxide, water, and a sulphate:



In addition to the above specialized properties, sulphuric acid shows all the properties of a typical strong acid.

Uses. Sulphuric acid is probably the most important chemical compound known. It is used in practically every industry. Regarding its use, the statement is often made that “the civilization of a country is measured by the amount of sulphuric acid it uses”.

Because of its *dehydrating action*, sulphuric acid is used to char and remove certain organic impurities in refining petroleum. It is important also in the preparation of most explosives to remove the water formed by the reaction, e.g.



If sulphuric acid were not used, the action could not continue because of the dilution caused by the water formed. Its dehydrating action is also employed in making photographic films. In the laboratory it is often used for drying gases.

Because of its *high boiling point*, sulphuric acid enters into the preparation of hydrochloric, nitric, and other less important acids.

In the steel industry, the acid is valuable for removing rust (*pickling*) before the metal receives a coating of enamel, zinc, or tin. Large quantities are used in tanning leather, converting starch into glucose, and in the manufacture of rayon from wood pulp. The acid is also used in making storage batteries.

Many thousands of tons of sulphuric acid go annually into the preparation of fertilizers, chief of which are superphosphate of lime and ammonium sulphate.

Sulphates. Many sulphates occur as *natural* deposits; chief of these is gypsum, important in the building trade and in the manufacture of plaster of Paris. Another natural deposit is the mineral barytes, the sulphate of barium, used in making paints and in weighting paper and rubber. Still another is Epsom salt, a hydrated magnesium sulphate, used as a cathartic. Sulphates *manufactured* by using sulphuric acid include Glauber's salt, an important medicine; alum, a styptic; aluminum sulphate, a mordant and a water clarifier; bluestone, a valuable ingredient in copper plating, fungicides, and a preservative of wood and hides; and green vitriol, a hydrated ferrous sulphate used in ink and dye manufacture and in tanning leather.

Soluble sulphates can be detected by dissolving in water and adding a barium chloride solution. However, because both sulphates and sulphites give white precipitates of barium sulphate and barium sulphite respectively, a confirmatory test is necessary. On the addition of dilute hydrochloric acid, barium sulphite dissolves, but the barium sulphate precipitate, being insoluble in dilute hydrochloric acid, remains. The above **tests** are used to identify sulphates and sulphites.

EXERCISE

A

1. Give an account of the occurrence of sulphur in both the free and the combined states.

2. Describe how flowers of sulphur and roll sulphur are obtained from volcanic deposits.

3. (a) Describe the Frasch process of mining sulphur, and show how Frasch connected two important facts in developing his method. (b) Why is the compressed air heated in the Frasch process? (c) Why is the melted sulphur made to rise in the intermediate rather than in the other pipes?

4. (a) Name and describe the allotropic forms of sulphur and outline briefly a method for preparing a sample of each from roll sulphur. (b) Why is it impossible to purchase sulphur in either the monoclinic or the plastic form?

5. State five important uses of sulphur. In your opinion which of these is the most important in your community? Give reasons for your answer.

6. Using a diagram to illustrate your answer, describe a laboratory method of preparing and collecting hydrogen sulphide. Write the equation to represent the reaction.

7. (a) Describe the visible changes that take place when hydrogen sulphide is passed into a solution of (i) cupric chloride; (ii) zinc chloride; (iii) lead nitrate. (b) Write the equation for each of the above reactions.

8. Write the equation for the incomplete combustion of hydrogen sulphide. What are the relative volumes of hydrogen sulphide and oxygen necessary for complete combustion?

9. What visible change occurs when moist hydrogen sulphide and sulphur dioxide are mixed? What property of hydrogen sulphide is illustrated by this reaction? Write the equation for the reaction.

10. Why is hydrogen sulphide less dangerous as a poisonous gas than is carbon monoxide?

11. Account for the precipitate of sulphur found in a water solution of hydrogen sulphide (hydrosulphuric acid) which has been standing for some days. What would be the odour of the contents? Write the equation for the reaction that has taken place.

12. (a) Describe the steps necessary for the preparation of hydrogen sulphide from sulphur, iron filings, and hydrochloric acid and write the equations that represent the chemical reactions. (b) How could you prove the presence of both hydrogen and sulphur in hydrogen sulphide gas?

13. Write the equations representing the reaction between hydrosulphuric acid and (a) sodium hydroxide; (b) ammonium hydroxide. Name the salt formed in each case.

14. Using a diagram to illustrate your answer describe a laboratory method of preparing and collecting sulphur dioxide. Write the equation to represent the reaction.

15. Sulphur dioxide may act as either a reducing agent or an oxidizing agent. Write an equation to represent each of these reactions. Which property do you consider the more important? Give a reason for your selection.

16. (a) Explain the bleaching action of sulphur dioxide. (b) Compare the bleaching action of sulphur dioxide with that of chlorine. (c) Straw bleached with sulphur dioxide in time returns to its natural yellow colour. Explain.

17. What properties of sulphur dioxide make it useful as a refrigerant?

18. (a) Name and write the formula for the acid formed when each of the following is dissolved in water: hydrogen sulphide, sulphur dioxide, sulphur trioxide. (b) Which of the above compounds are acid anhydrides?

19. Discuss the dechlorination of the water supply of a large city under the headings: (a) Reason for dechlorination. (b) Why the use of sulphur dioxide is effective.

20. (a) Describe the contact method for making sulphuric acid. (b) Compare the sulphuric acids made by contact and chamber methods as to raw materials used in the preparation, the purity of the acid formed, and the uses of the respective acids.

21. List (a) the physical properties and (b) the chemical properties of sulphuric acid.

22. What is the correct method for diluting concentrated sulphuric acid? Why?

23. Account for (a) the darkened rings formed on wood under bottles of concentrated sulphuric acid; (b) the increase in volume when a bottle of concentrated sulphuric acid is left unstoppered; (c) the terrible burns produced by boiling concentrated sulphuric acid.

24. (a) Write equations to represent the action of concentrated sulphuric acid on (i) sugar; (ii) charcoal; (iii) copper. (b) Write the equation for the action of dilute sulphuric acid on zinc.

25. What property of sulphuric acid is made use of in (a) the refining of petroleum; (b) the manufacture of nitroglycerine; (c) the manufacture of other acids; (d) the making of lead storage batteries; (e) the pickling of metals?

26. (a) Why is concentrated sulphuric acid known as *oil of vitriol*? (b) Write the names and the formulae of six important sulphates.

27. Barium chloride solution is used as a test to identify both a sulphate and

a sulphite. (a) Write the equation for each of the above reactions. (b) Why is a confirmatory test necessary to distinguish between the two types of salts? (c) Write the equation to illustrate the confirmatory test for the sulphite.

28. Sulphuric acid may act as an acid, as a dehydrating agent, and as an oxidizing agent. Describe two experiments in each case to illustrate each of these properties.

29. Sulphuric acid has been called "the king of chemicals." Why is this title appropriate?

B

1. What weight of sulphur is required to produce 50 grams of sulphur dioxide?

2. (a) What weight of ferrous sulphide is required to produce 68 grams of hydrogen sulphide? (b) What volume would the hydrogen sulphide occupy at S.T.P.?

3. What volume of hydrogen sulphide measured at 20° C. and 750 mm. pressure could be prepared from 11 grams of ferrous sulphide?

4. What volume of sulphur dioxide would be formed by the complete combustion of 5 litres of hydrogen sulphide if both gases are measured at the same temperature and pressure?

5. What weight of sodium sulphite will be required to produce 3 litres of sulphur dioxide measured at 18° C. and 765 mm. pressure?

6. The reaction of hydrogen sulphide and sulphur dioxide may be expressed by the following equation:



(a) What volume of hydrogen sulphide is required to react completely with 20 litres of sulphur dioxide (both gases measured at the same temperature and pressure)? (b) What volume of sulphur dioxide measured at 20° C. and 750 mm. pressure is required to produce 10 gm. of sulphur in the above reaction?

CHAPTER 20

Salt and Its Place in Industry

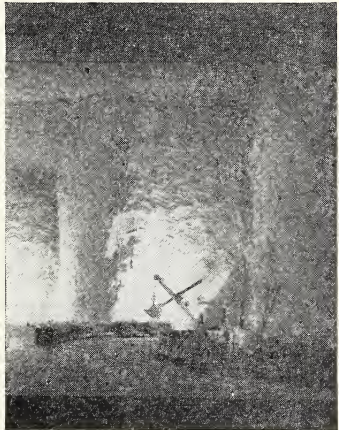
Can that which is unsavoury be eaten without salt?

JOB VI: 6.

Salt, or sodium chloride (NaCl), is one of the few vitally essential minerals taken from the earth. Probably the details of Man's discovery of salt will always be a matter of conjecture. Salt may have been first discovered as an outcropping of a white crystalline rock, or one of our far-removed ancestors, having eaten some sea-weed cast upon the shore, may have enjoyed its salty flavour. Later, perhaps, a salt supply was derived from crude deposits remaining after pools of sea-water had evaporated under the intense heat of the sun.

COMMON SALT (NaCl)

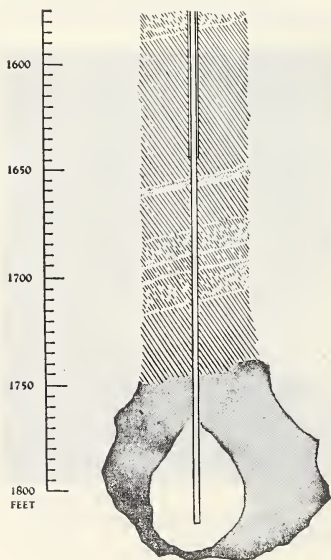
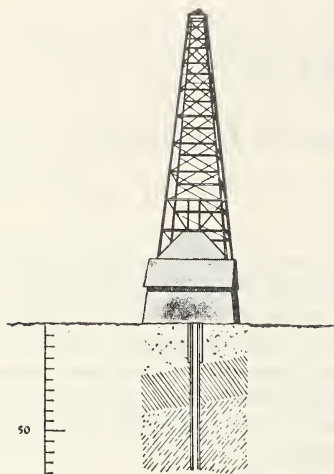
Occurrence. The effect of salt on the taste of food increased the demand for it, and historians inform us that many great centres of civilization came into being because of barter with salt. Salt occurs in solution in the ocean, in salt lakes, in salt wells, and as a solid in rock-salt deposits. Nature has liberally distributed salt throughout Canada, particularly in Ontario. In southwestern Ontario, in the region of the Detroit River, the deposits of rock-salt are so vast that experts estimate them sufficient to serve the world for 90,000 years. These huge deposits indicate that at some time in the past this area was covered with sea-water. These salt beds, covering an area of at least 3,000 sq. mi., are about one thousand feet below the surface of the earth and vary in thickness from 100 feet to 230 feet.



International Salt

Fig. 20.1. Mining salt from a subterranean deposit.

Commercial recovery. The salt of subterranean deposits may be obtained either by digging to the deposit and mining it directly, or

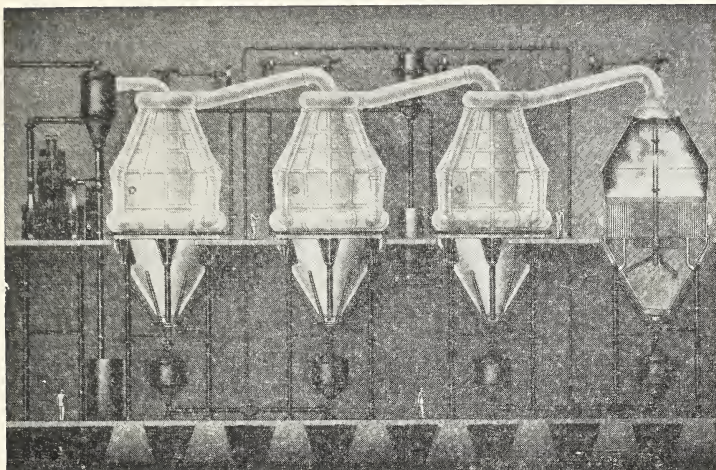


International Salt

Fig. 20.2. A salt well.

by drilling wells to the bottom of the salt bed and dissolving the salt with water. The latter method is the common one in most modern salt plants. Water, forced under a pressure of 175 pounds per square inch down a large outer pipe, dissolves the salt, and the pressure forces the resulting brine up a smaller, inner pipe (Fig. 20.2). Huge settling tanks, holding thousands of gallons each, receive the brine, and, after the insoluble materials settle, the clear salt solution flows to a series of vacuum evaporators (Fig. 20.3) for crystallization.

Live steam is admitted into the steam chamber of the first pan where the brine starts to boil. The steam from it passes to the steam chamber of the second pan of comparatively cool brine where it condenses and gives up its heat to the brine. This condensation of steam creates a partial vacuum extending to the first pan. Soon the brine in the second pan starts to boil, and the resultant steam passes on to the steam chamber of the third pan where it condenses and heats the brine in this pan. This creates a partial vacuum in the second pan. A stream of cold water, falling through the vacuum pump attached to the third pan, condenses the steam drawn off by the pump, thus creating and sustaining a high degree of vacuum in the third pan. The



International Salt Company

Fig. 20.3. A series of four vacuum evaporators that remove water from brine obtained from a salt well.

brine soon starts to boil without getting more than fairly warm. In a partial vacuum, water boils at a reduced temperature; thus by reducing the pressure successively from one evaporator to the next, the original heat is used three, or even four times as in Fig. 20.3.

The moist crystallized salt is removed automatically to a special fine-screen filter where continuous suction removes most of the water. It is then transferred to large revolving cylinders through which air, heated well above the boiling point of water, is forced until the salt is perfectly dry and ready for screening according to the size of the crystals.

The finest crystals are used for table salt, and the larger ones go into the production of dairy salt, or they may be compressed into blocks for "cattle licks" or into small tablets for human consumption. Millions of these tablets are used annually in Canadian factories to prevent heat cramps and heat prostration. Larger tablets are important in the canning industry where uniformity of flavour is secured when one tablet is deposited in every can by automatic dispensing machines.

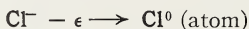
A single crystal of salt assumes the shape of an almost perfect cube. Although each crystal is transparent, a mass of crystals appears white. Salt is almost as soluble in cold water as it is in hot (see Solubility

Curve, p. 77). It melts at the rather high temperature of 805°C. , and in this fused condition conducts a current of electricity, thus indicating the existence of free sodium ions and chloride ions (Chapter 16).

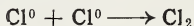
Electrolysis of salt solution. When sodium chloride is dissolved in water, it dissociates into positively charged sodium ions (Na^{+}), and negatively charged chloride ions (Cl^{-}).



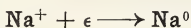
When an electric current is passed through this solution, the chloride ions (anions) are attracted to the positively charged anode where each gives up its extra electron and becomes a neutral atom of chlorine.



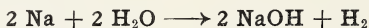
The chlorine atoms immediately combine in pairs to form chlorine molecules and bubbles of chlorine gas arise and escape at the anode.



The sodium ions (cations) are attracted to the negatively charged cathode where each ion receives an electron and becomes a sodium atom.



The atoms of sodium, thus formed, have all the properties of sodium "metal", and unlike sodium ions they cannot exist in the presence of water. The sodium atoms immediately react with the water to form sodium hydroxide and hydrogen. The latter rises as bubbles from the cathode.



Hence the electrolysis of a salt solution results in chlorine gas forming at the anode, while hydrogen gas and sodium hydroxide solution gather at the cathode. Both of these gases can be collected, and as the action continues the solution becomes more and more concentrated with sodium hydroxide.

When the solution of sodium hydroxide is evaporated to dryness, a white deposit of solid sodium hydroxide, commonly known as caustic soda, remains.

In the electrolysis of a solution of sodium chloride, chlorine is a **primary product** because it forms directly from ions losing their electrical charges. Hydrogen and sodium hydroxide are **secondary products** because they are formed by a secondary reaction.

There is another, and possibly more exact, explanation of electrolysis of brine involving the ionization of water. Water provides a very small quantity of H^{+} ions and OH^{-} (hydroxyl) ions. A salt solution

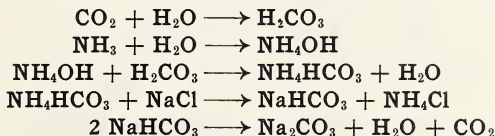
contains Na^+ , Cl^- , H^+ , and OH^- ions. The positively charged ions Na^+ and H^+ are attracted to the cathode, and the negatively charged Cl^- and OH^- ions to the anode. Of the positive ions, H^+ ions accept electrons more readily than do the Na^+ ions, so only H^+ ions are neutralized. The Na^+ is unaffected. Similarly, Cl^- is neutralized at the anode and the OH^- remains unaffected. Thus hydrogen is liberated at the cathode and chlorine at the anode. The Na^+ and OH^- ions unite to form NaOH in solution.

Caustic soda is deliquescent, dissolves readily in water liberating considerable heat, and produces an alkaline solution. It has many uses in industry.

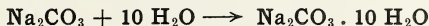
The uses of hydrogen have been given in Chapter 6 and the properties and uses of chlorine will be found in the following chapter. The hydrogen and chlorine are sometimes combined to produce hydrogen chloride of great purity. If the market warrants, the hydrogen may be combined with nitrogen to form ammonia and the chlorine liquefied.

THE SODA INDUSTRY

Sodium bicarbonate, or baking soda, and sodium carbonate, or sal soda, are made directly from sodium chloride by a continuous industrial process, the **Solvay process**, requiring rather elaborate apparatus. A saturated water solution of salt, is further saturated with both ammonia gas and carbon dioxide gas in specially constructed towers. The carbon dioxide, under pressure, dissolves forming carbonic acid, and the ammonia readily dissolves forming ammonium hydroxide. The acid and the base react to produce a solution of ammonium bicarbonate in water. The ammonium bicarbonate reacts with the salt solution to form sodium bicarbonate and ammonium chloride. The sodium bicarbonate, being insoluble in the concentrated salt solution, precipitates out, and is heated to convert it into sodium carbonate.



Washing soda (sodium carbonate decahydrate) is obtained by allowing a solution of sodium carbonate to evaporate slowly.



Pure sodium bicarbonate is made by bubbling carbon dioxide through a solution of sodium carbonate.



HYDROGEN CHLORIDE (HCl)

Preparation. Hydrogen chloride may be produced by direct union of the hydrogen and the chlorine resulting from the electrolysis of a salt solution. However, by far the most common method of preparation in both industry and the laboratory is by the treatment of sodium

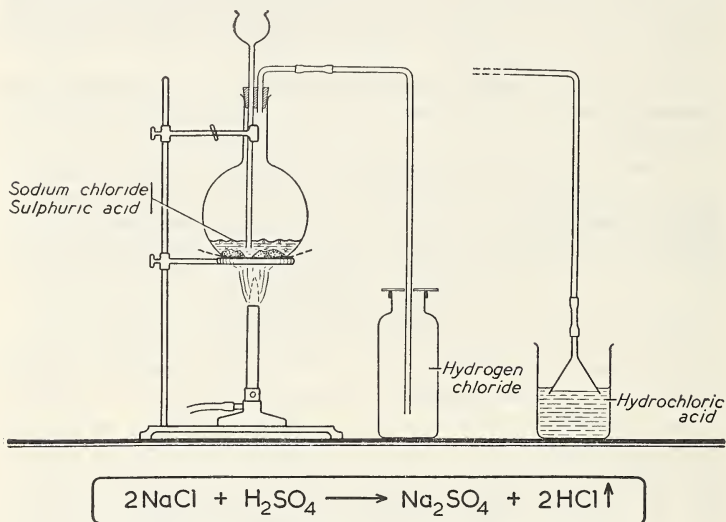
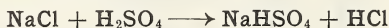


Fig. 20.4. The laboratory preparation and collection of hydrogen chloride.

chloride with concentrated sulphuric acid (Fig. 20.4). The reaction may take place in two definite stages:



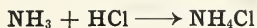
At higher temperatures and with an excess of salt:



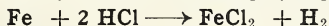
Properties. Hydrogen chloride is a colourless gas, denser than air, and it has a very irritating, sharp, choking odour. It is extremely soluble in water, one volume of water at 20° C. dissolving 442 volumes of the gas. Its great solubility is evidenced by the way in which it “fogs the breath”. It is so soluble that it will take water vapour from moist air to form a solution with water, thus forming a cloud.

An exothermic reaction takes place when hydrogen chloride gas and

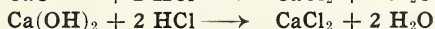
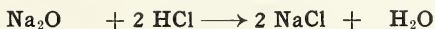
ammonia gas are mixed to produce dense white clouds of solid ammonium chloride.



As a "dry" gas, hydrogen chloride is not very active, but its water solution, known as **hydrochloric acid** is one of the strongest acids. It reacts vigorously with all metals more active than copper. In each reaction, hydrogen is produced.



Oxides of metals and their corresponding hydroxides react with hydrochloric acid producing salts and water.



Hydrochloric acid reacts with several oxidizing agents liberating chlorine gas. It reacts with carbonates to produce carbon dioxide, and with sulphites to produce sulphur dioxide.

Tests. The best test for hydrogen chloride makes use of its reaction with ammonia gas. If a glass rod, dipped in ammonium hydroxide, is lowered into a bottle of hydrogen chloride, dense white fumes of ammonium chloride result.

Another test identifying the gas as a chloride lies in observing its effect on a solution of silver nitrate. A white precipitate of silver chloride that quickly coagulates and turns dark in colour, when exposed to light, confirms the presence of a chloride.

Uses. Hydrochloric acid is used in soldering to dissolve oxides from metallic surfaces. It is valuable in the laboratory in the preparation of chlorine gas, and also as an active acid. It is useful in converting animal skins and bones into gelatin and glue. It acts as a catalyst in the hydrolysis of corn starch into glucose or corn syrup. A considerable

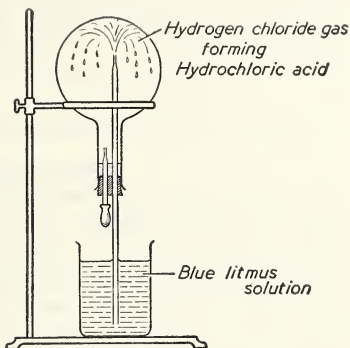
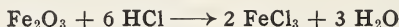


Fig. 20.5. Hydrogen chloride fountain. Hydrogen chloride is so soluble that when a few drops of water are forced by a dropper into a flask with the gas, the hydrogen chloride dissolves so rapidly that it creates a partial vacuum in the flask. Air pressure forces the blue litmus solution up the tube to form a "red" fountain.

amount of hydrochloric acid is of use in cleaning rust off iron and steel, in preparing fabricated articles for galvanizing, tinning, or electroplating.



The ferric chloride produced is soluble in water.

USES OF COMMON SALT

The prime household uses of salt are for seasoning and preserving food. It is also serviceable in ice-cream freezers, in the removal of ice from sidewalks, and as a dentifrice.

Salt is absolutely essential in all diets. Many farmers preserve fresh meat by salting it, and the use of smoked salt enhances the flavour. Salt, used in storage of hay crops, accomplishes three things, viz. it adds to the hay's palatability; it promotes better curing; and it reduces the danger of heating and spontaneous combustion.

Industry has many uses for salt. Food industries use considerable quantities of it for curing, pickling, preserving and seasoning. Large amounts of salt have their place in the dyeing and finishing of textiles. Zeolite water-softeners require salt to regenerate the zeolite. Raw skins are prepared with salt for the tanning process. In the manufacture of artificial ice, salt brine is the common cooling medium. Salt and ice are used to obtain and maintain the low temperatures required in some refrigerator cars for the transportation of perishable food products.

Salt is the source from which most sodium compounds are derived. Among these are sodium hydroxide, sodium bicarbonate, sodium carbonate, sodium sulphate, and sodium hypochlorite. Salt is also used in the production of chlorine, hydrochloric acid, hydrogen, synthetic ammonia, nitric acid, soap, glass, ceramics, and paper and it is equally indispensable in the refining of petroleum.

EXERCISE

A

1. (a) Give three natural sources of common salt. (b) What historical role has been played by common salt? (c) Describe the salt deposit located in southwestern Ontario. (d) What method is used to recover the salt found in Ontario? How is this salt refined?

2. List five properties of sodium chloride.

3. (a) Using equations to illustrate your answer, describe and explain the electrolysis of a common salt solution. (b) In any electrolysis, what is meant by a primary product and a secondary product? (c) In the electrolysis of brine, which are the primary and which the secondary products? (d) State two uses for each of the products resulting from the electrolysis of brine.

4. (a) Using equations to illustrate your answer, describe concisely the Solvay method for the manufacture of sodium carbonate. (b) What is the formula of washing soda crystals? How are these crystals obtained from anhydrous sodium carbonate? Write the equation. (c) What name is given to this type of chemical reaction?

5. Using a diagram to illustrate your answer, describe the laboratory method for the preparation and collection of hydrogen chloride. Write two equations that could represent the reaction.

6. (a) List five properties of hydrogen chloride. (b) Select two of these properties that could be used as tests for the gas.

7. (a) What is a water solution of hydrogen chloride called? (b) List six properties of this solution.

8. Write equations to represent the reaction of hydrochloric acid on (a) magnesium; (b) zinc; (c) iron.

9. Write equations to represent the action of hydrochloric acid on (a) calcium oxide; (b) sodium hydroxide; (c) calcium carbonate; (d) sodium sulphite.

10. Give in detail the best laboratory test for hydrogen chloride.

11. List five uses of hydrochloric acid.

12. What is the role played by common salt in (a) the home; (b) the dairy industry; (c) the storage of hay crops; (d) water softening; (e) refrigeration; (f) chemical industry?

13. Name twelve chemical compounds other than those resulting from the Solvay process that may be made from common salt.

B

1. From the formula of common salt, find its percentage composition.

2. When sodium chloride or potassium chloride is heated with sulphuric acid, hydrogen chloride is obtained. If the cost of both salts were the same, which would be the cheaper method of producing hydrogen chloride? Explain.

3. (a) Which would be more economical, 10 pounds of washing soda crystals at six cents per pound, or 5 pounds of anhydrous sodium carbonate at twelve cents per pound? (b) How could washing soda crystals be converted into baking soda? What weight of baking soda would be obtained from 10 pounds of the crystals?

4. How many litres of hydrogen chloride measured at S.T.P. will be produced from the action of sulphuric acid on 23.4 gm. sodium chloride?

5. In the electrolysis of a common salt solution, what volume of chlorine measured at 20° C. and 750 mm. pressure could be obtained from the decomposition of 58.5 gm. sodium chloride? What weight of sodium hydroxide would be produced?

CHAPTER 21

The Halogens

But dephlogisticated marine acid (chlorine), which destroys all vegetable colours more or less easily, acts in a different manner on animal colours.

M. BERTHOLLET

Fluorine, chlorine, bromine, iodine, and astatine produce substances resembling common salt in composition and chemical action, and hence are known as **halogens**, a name meaning *formers of sea salt*, and the metallic compounds of halogens are called **halides**. The halogens are univalent and have the most pronounced non-metallic characteristics of any related group of elements.

FLUORINE

Fluorine, the most active halogen, has been called "the devil element" because of its unruly nature. Only recently has it been harnessed for the service of mankind.

Fluorine is a pale greenish-yellow gas, slightly denser than air and quite poisonous. Henri Moissan isolated it in 1886, but almost sixty years passed before scientists solved the problems of producing it in large quantities and handling it safely.

As an element, it has few uses, but compounds of fluorine are becoming more important. Hydrofluoric acid is one of the most corrosive compounds known, and although used for etching glass is employed more extensively in the manufacture of a series of complex organic compounds called **freons**. The most widely used member of this series is a non-corrosive, non-toxic, non-inflammable, and almost colourless gas. It can be readily liquefied under moderate pressure and used as a refrigerant. "Aerosol" insecticide is a solution of pyrethrum in freon. Fluorine compounds are also of use in the manufacture of rodenticides and a few plastics. Fluorides are proving effective in anti-caries.

CHLORINE

Chlorine was first prepared by a Swedish chemist Karl Wilhelm Scheele in 1774 from manganese dioxide and hydrochloric acid, but

it was not recognized as an element until 1810 when Sir Humphry Davy named it *chlorine* (*chloros*, green).

Occurrence. Chlorine, the second most active non-metallic element, is never found in the uncombined, or free, state. It most commonly occurs as a chloride in combination with sodium, potassium, or magnesium. Sodium chloride is the cheapest, and by far the most abundant chloride.

Laboratory preparation. The most satisfactory laboratory method of producing chlorine is by the oxidation of hydrochloric acid. If manganese dioxide is used as the oxidizing agent, it is necessary to warm the generator gently (Fig. 21.2).

Effervescence occurs and a greenish-yellow gas soon fills the collecting bottle. The colour of the gas makes it easy to determine when the container is full of chlorine.

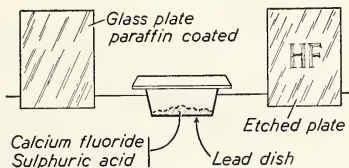
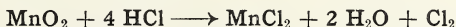
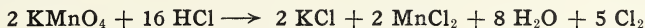


Fig. 21.1. Etching glass with hydrofluoric acid. The letters, formed by removing paraffin from the glass surface, are permanently etched on the glass by the acid vapour produced by the action of sulphuric acid on the fluoride.



If potassium permanganate is the oxidizing agent, no heat is required.



It is also possible to liberate chlorine from sodium chloride by gently heating a mixture of the salt with manganese dioxide and concentrated sulphuric acid. However, the chlorine so produced is not entirely free from hydrogen chloride.

Commercial preparation. Chlorine is one of the products resulting from the electrolysis of a solution of sodium chloride (Chapter 20).

Physical properties. Chlorine is a poisonous gas of greenish-yellow colour and very irritating odour. It is denser than air (71:28.9), and liquefies at room temperature (20° C.) if subjected to a pressure of 6.6 atmospheres. At atmospheric pressure, chlorine turns to a liquid at -34.6° C. and freezes at -102° C. It is moderately soluble in water, 1.47 gm. dissolving in 100 gm. water at 0° C.

Chemical properties. Of the non-metals, chlorine is second only to fluorine in chemical activity. This great activity is attributed to the eagerness with which the chlorine atom gains an electron to complete its third (valence) ring.

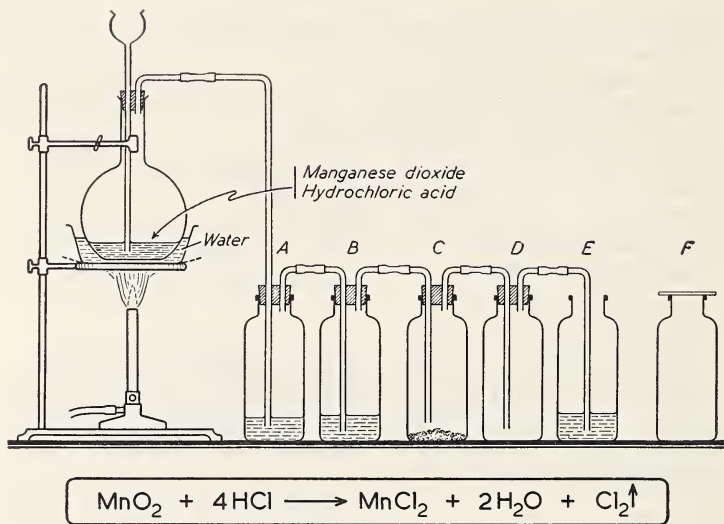
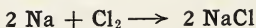
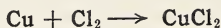


Fig. 21.2. The laboratory preparation and collection of chlorine. *A*, contains water to prepare chlorine water and to dissolve any hydrogen chloride that may be driven over. *B*, contains concentrated sulphuric acid to dry the chlorine. *C*, contains slaked lime for making a sample of bleaching powder. *D*, is for the collection of pure dry chlorine. *E*, contains a solution of sodium thiosulphate to prevent the escape of chlorine gas into the laboratory. *F*, a bottle of dry chlorine that has been filled at *D*.

1. *Active metals.* Active metals, such as sodium and potassium, unite directly with chlorine to form chlorides. A thin piece of warm sodium, held in a bottle of chlorine, burns with a brilliant yellow flame to produce a fluffy white mass of pure sodium chloride.

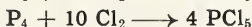
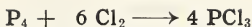


2. *Less active metals.* When copper foil is heated and lowered into a bottle of chlorine, it glows brightly to produce greenish-yellow cupric chloride.

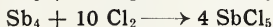
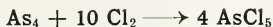
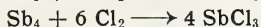
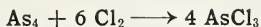


Even gold and platinum react moderately with chlorine.

3. *Non-metals.* With a brilliant yellow flame, yellow phosphorus and chlorine unite directly producing a dense white cloud of phosphorus trichloride and phosphorus pentachloride.



Powdered arsenic and powdered antimony, when dropped into chlorine, produce a brilliant display of scintillating sparks and then leave behind a white cloud of their respective trichlorides and pentachlorides.



4. *Hydrogen.* Chlorine displays a remarkable affinity for hydrogen, the atoms of each sharing an electron in the formation of a hydrogen chloride molecule. A jet of hydrogen, burning with a pale-blue flame in air, continues to burn when lowered into a container of chlorine, but it burns with a peculiar luminous flame. Mixtures of the two gases show no appreciable action while in the dark, but they explode violently on exposure to sunlight or to light from burning magnesium.

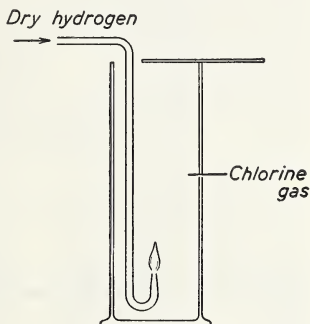
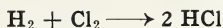
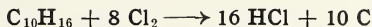


Fig. 21.3. Hydrogen burning in chlorine. The product of this combustion is hydrogen chloride.



5. *Hydrocarbons.* Hydrocarbons are organic compounds containing only hydrogen and carbon. Turpentine ($\text{C}_{10}\text{H}_{16}$) and paraffin wax are two examples of hydrocarbons useful for illustrating the affinity of chlorine for hydrogen. A loose roll of filter paper, soaked with warm turpentine and pushed into a large bottle of chlorine, will ignite with explosive vigour to create an orange-coloured flame and a spectacular smoke cloud of black particles of carbon.



When a lighted candle or wax taper is lowered into a bottle of chlorine, it continues to burn with a peculiar yellow flame, and produces dense clouds of black specks of carbon. In each of these experiments, the hydrogen chloride produced may be identified by the "fogging of the breath" when the breath is blown across the mouth of the bottle. These experiments are of special interest as examples of *combustion without oxygen*.

6. *Water.* The bleaching action of chlorine in the presence of moisture is further proof of its affinity for hydrogen. When chlorine reacts with water, a series of chemical actions take place to form *atomic* oxygen. The probable reactions taking place are represented thus:

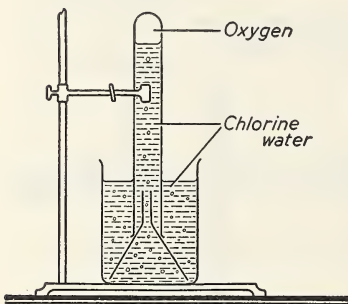
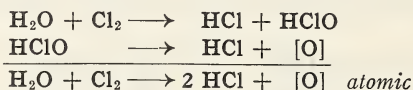


Fig. 21.4. When a solution of chlorine and water is allowed to stand in sunlight, oxygen is liberated from the water and hydrochloric acid remains.

The unstable hypochlorous acid decomposes, with the liberation of the active atomic oxygen, which in turn is responsible for both bleaching action and germicidal action. Chlorine is known as an oxidizing agent because it makes atomic oxygen available for oxidizing colouring matter or bacteria. Bleaching with chlorine is in direct contrast to bleaching with sulphur dioxide because sulphur dioxide, in the bleaching process, acts as a reducing agent by removing oxygen.

If freshly prepared chlorine water is allowed to stand, the atomic oxygen becomes molecular and loses its ability to bleach; a solution of hydrochloric acid remains.

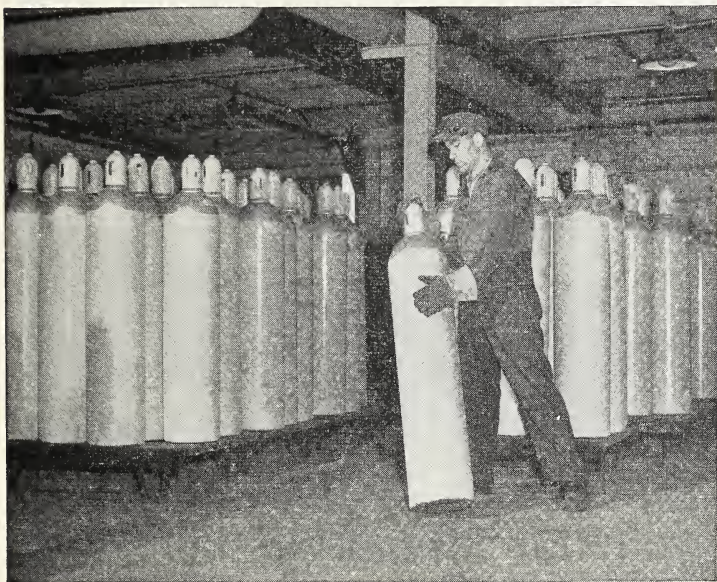


Uses. *As a bleaching agent.* A high percentage of the chlorine of industry is used to bleach wood pulp and vegetable fibres. Chlorine, however, permanently injures fibres of animal origin, e.g. wool and silk. Even vegetable fibres cannot be exposed to chlorine for too long a time. Precaution is taken to remove excess chlorine from the fibres by washing them first in a solution of an *antichlor*, and then in clear water. The most common antichlors are sodium sulphite, sodium thiosulphate, and hydrogen peroxide.

As a germicide. One part by weight of chlorine in one million parts of drinking water kills all harmful germs. Chlorination of drinking water is as important a safety measure as is pasteurization of milk. The use of chlorine in swimming pools and sewage disposal plants is

familiar to everyone. A few Canadian cities now use chlorine dioxide as a source of chlorine for water purification.

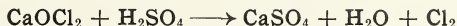
Bleaching powder is made by passing chlorine over calcium hydroxide.



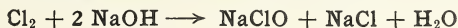
Canadian Industries Limited

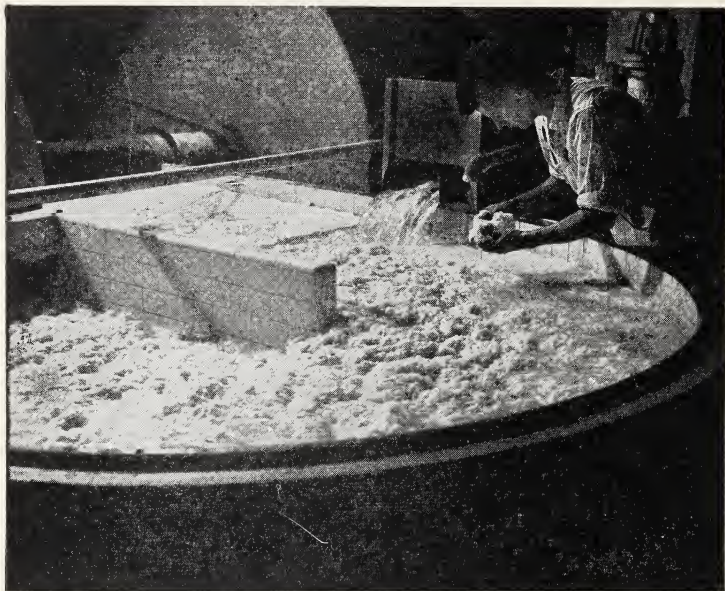
Fig. 21.5. Cylinders, containing 150 pounds of liquid chlorine each, are readied for shipment from the chemicals plant of Canadian Industries Limited at Cornwall, Ontario.

Bleaching powder (chlorinated lime) is sometimes incorrectly called "chloride of lime". When it is treated with dilute acids, more than 99% of the available chlorine is liberated. This property makes it useful in industry for bleaching and as a disinfectant.



Javelle water. Although made by various methods, javelle water commonly used for whitening clothes, consists essentially of a mixture of the solutions of sodium hypochlorite and sodium chloride. The manufacture of javelle water by passing chlorine into a caustic soda solution is represented by the following equation:





Canadian Industries Limited

Fig. 21.6. Paper pulp being bleached with chlorine.

The unstable sodium hypochlorite produces atomic oxygen that is responsible for the bleaching qualities.

Chloroform (CHCl_3), and *carbon tetrachloride* (CCl_4), in addition to many other compounds, owe their existence to chlorine.

Tests. The choking odour and the greenish-yellow colour of chlorine are quite characteristic and might be considered reliable tests, but they are not scientific. The best chemical test makes use of the fact that chlorine is much more active than iodine. When chlorine is bubbled into a solution of potassium iodide, the iodine is displaced, and as the free iodine goes into solution a rich brown colour occurs.



If a few drops of this brown solution are added to a colloidal solution of starch, a deep blue colour results. This test may be more easily made by using previously prepared **starch-iodized** paper.

BROMINE

Bromine is much too active an element to be found free in nature. Antoine-Jerome Balard, a young French chemist and pharmacist, discovered it in 1826. By adding chlorine to the salt brines obtained from the salt marshes near Montpellier, he produced a brownish-red liquid which he called "muride". The name for this new element was later changed to **bromine**, a word meaning *bad odour*.

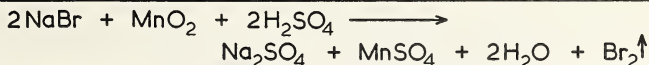
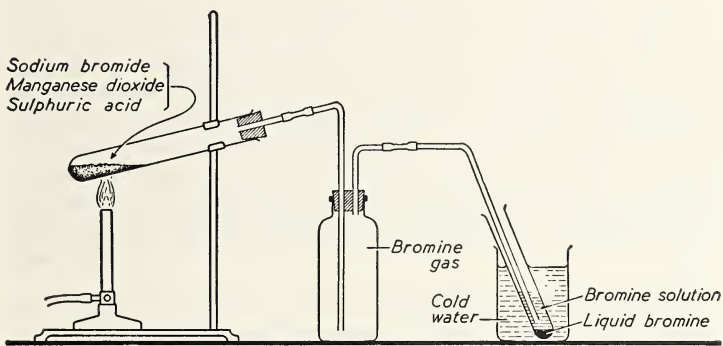


Fig. 21.7. The laboratory preparation and collection of bromine.

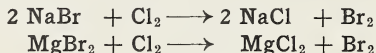
Occurrence. Bromine occurs in chemical combination with sodium, potassium, and magnesium. These salts are found in certain mineral springs, in the upper layers of beds of rock salt, and in sea-water.

Laboratory preparation. The usual method of preparing bromine is to release it from either sodium or potassium bromide by adding concentrated sulphuric acid to a mixture of the bromide and manganese dioxide and warming gently. If the reaction is carried out as shown in Fig. 21.7, a heavy brownish-red vapour fills the generator and gas bottle, and drops of liquid bromine condense in the cool receiver.



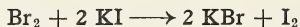
Commercial preparation. Bromine is obtained from the bromides in sea-water by displacement with chlorine. The procedure is modified

according to the concentration of the bromide, in most cases quite dilute. The displaced bromine dissolves in the solution and remains dissolved until driven out by a current of air in specially constructed towers. The resulting liquid bromine is concentrated by distillation.



Physical properties. Bromine, a deep brownish-red liquid, is the only element except mercury that is liquid at ordinary temperatures. It is quite volatile, producing a brownish-red, irritating, poisonous vapour. Caution must be exercised to keep bromine away from the skin because it causes severe burns. Liquid bromine has a density of 3.18 gm. per cc. at 0° C., a boiling point of 58.7° C., and a melting point of -7.3° C. It is more soluble in water than chlorine, 4.17 gm. dissolving in 100 gm. of water at 0° C. Bromine is quite soluble in organic solvents such as alcohol, carbon disulphide, and carbon tetrachloride, with each of which it forms a characteristic reddish-orange solution.

Chemical properties. Because the bromine atom is larger than the chlorine atom, the tendency to attract an electron to its outer orbit to complete the stable octet is not so great as is that of the chlorine atom. For this reason, the chemical activity of bromine is less than that of chlorine. Bromine, however, is very active, as shown by its ability to displace iodine from solutions of iodides.



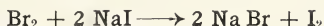
The bleaching properties of bromine, although not so pronounced as those of chlorine, are nevertheless impressive. Hydrogen requires a temperature of 200° C. to unite with bromine producing hydrogen bromide.

Both antimony and phosphorus burn spontaneously when placed in bromine vapour to form bromides, and most metals show the effect of being attacked by the vapour.

Uses. Bromine is used chiefly in the manufacture of many compounds. During the First World War, it was used in the manufacture of "tear gas", and in recent years in the preparation of ethylene dibromide ($\text{C}_2\text{H}_4\text{Br}_2$), and this in turn is used together with tetraethyl lead in anti-knock gasoline. Bromine is also used extensively to make silver bromide for sensitizing photographic gelatines, and in the manufacture of synthetic dyes and medicinal preparations.

Test. With starch "solution", bromine gives a distinctive reddish-

orange colour. More active than iodine, bromine will displace it from soluble iodides in solution.



This free iodine will give a characteristic deep-blue colour with starch "solution".

IODINE

In 1811, a Frenchman, Bernard Courtois, noticed that when the containers used to make saltpetre from the ashes of sea-weed, were cleaned with sulphuric acid, a beautiful violet-coloured vapour was produced. Courtois did not know that the sea-weed contained iodides from which a new and important element was soon to be isolated. His curiosity was sufficiently aroused, however, to cause him to tell the chemist, Gay-Lussac, about his observations. In 1813, Gay-Lussac was successful in producing the element **iodine**, the name of which was derived from the Greek word meaning *violet*.

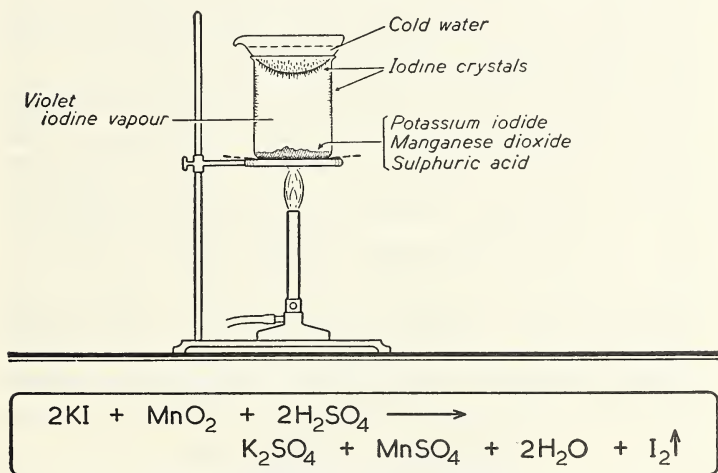
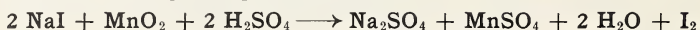


Fig. 21.8. The laboratory preparation and collection of iodine.

Occurrence. Although iodine is less active than either chlorine and bromine, it is much too active to be found free in nature. Kelp, a sea-weed containing sodium iodide, served as the original source of all iodine. The chief present-day sources of iodine are the iodides in brine

wells of California and Louisiana, and sodium iodate (Na IO_3), contained in the Chile saltpetre deposits.

Laboratory preparation. In the laboratory, iodine is prepared in much the same way as is bromine; sodium or potassium iodide replaces the corresponding bromides.



When these chemicals are gently heated, a dense violet-coloured vapour is produced, and this readily sublimes on a cold surface into flat, shiny, steel-grey crystals.

Commercial preparation. There are four common industrial methods used in obtaining iodine.

1. Using kelp rather than the metallic halide in the method mentioned above.

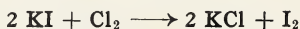
2. Chlorine, added to a solution of an iodide, displaces the slightly soluble iodine which may be filtered off and dried.

3. Silver nitrate, added to a solution of an iodide, causes yellow silver iodide to be precipitated. Both the silver and the iodine are recovered by subsequent treatment with iron and chlorine.

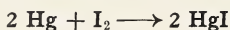
4. Sodium iodate, obtained from Chile saltpetre deposits, is treated with sodium bisulphite solution and free iodine is liberated.

Physical properties. The violet-coloured iodine vapour has a most irritating odour, and when cooled sublimes to form flat steel-grey crystals. Iodine melts at 113.5°C ., and has a specific gravity of 4.93. If heated carefully, the solid can be converted directly to the vapour, and this vapour, on meeting a cold surface, reforms by *sublimation* into the crystalline state without at any time entering the liquid state. Iodine is almost insoluble in water, 0.019 gm. dissolving in 100 gm. of water at 0°C . It dissolves readily in many organic solvents. Both alcohol and ether each produce a brown solution, whereas carbon tetrachloride, carbon disulphide, and chloroform give violet-coloured solutions.

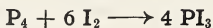
Chemical properties. Because iodine is the least active halogen, both chlorine and bromine will displace it from iodides.



Iodine combines directly with mercury to form red mercuric iodide.



Non-metallic yellow phosphorus unites directly to form dark-red phosphorous iodide.



Uses. Iodine is used in the manufacture of dyes, drugs, and photographic supplies. Tincture of iodine, a 2% to 3% solution of iodine in a mixture of ethyl alcohol and potassium iodide, and iodoform (CHI_3) are widely used as antiseptics. Small quantities of potassium iodide are added to common salt as a preventative of goitre. Salt treated in this manner is known as "iodized salt".

Test. Free iodine in contact with starch "solution" produces an intense blue colour. This colour provides a test for either iodine, or starch, and will detect as little as one part of iodine in five million parts of solution.

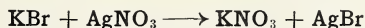
TESTS FOR CHLORIDES, BROMIDES, and IODIDES

1. A clear colourless solution known to be that of a chloride, a bromide, or an iodide, can readily be identified by bubbling chlorine gas into the solution. If it is a chloride, the only visible change will be that the solution gradually acquires the greenish-yellow colour of chlorine. If it is a bromide, the solution will turn a brownish-red colour because of the liberation of free bromine which dissolves in the solution. The presence of bromine can be confirmed by the addition of carbon tetrachloride, which gives a reddish-orange colour. If an iodide, the solution turns a dark-brown colour due to the liberation of free iodine which dissolves in the solution. The presence of iodine can be confirmed by the addition of starch "solution" which gives the characteristic blue colour, or by adding either carbon tetrachloride or carbon disulphide, which give a violet-coloured solution.

2. When silver nitrate solution is added to a solution of a chloride, a curdy white precipitate of silver chloride is formed:



This precipitate darkens rapidly on exposure to sunlight and *completely dissolves* on the addition of ammonium hydroxide. With a bromide solution, silver nitrate produces a cream-coloured precipitate, and this also darkens on exposure to light, but on the addition of ammonium hydroxide only *partially dissolves*:



With an iodide solution, silver nitrate produces a pale-yellow precipitate which also darkens on exposure to light, but is *insoluble* in ammonium hydroxide:



The colour changes in these tests are easily distinguished when the

three are viewed together, but the use of ammonium hydroxide is essential as a confirmatory test.

Chlorides, bromides, and iodides are not the only substances that form precipitates with a silver nitrate solution. A chemical test must be *specific*. Fortunately, silver chloride, silver bromide, and silver iodide are all insoluble in dilute nitric acid, while other precipitates that might be mistaken for them (e.g. silver carbonate, silver phosphate) readily dissolve when dilute nitric acid is added.

EXERCISE

A

1. (a) Name five members of the halogen family. (b) What does the word *halogen* mean? What are the compounds of the halogens called?

2. (a) Why is fluorine sometimes called "the devil element"? (b) Give the commercial names of two compounds of fluorine. (c) State five commercial uses of fluorine compounds.

3. Using a diagram to illustrate your answer, describe a laboratory method for the preparation and collection of chlorine. Write the equation for the reaction.

4. List (a) five physical and (b) six chemical properties of chlorine.

5. Using the electron theory, explain the great chemical activity of chlorine as a non-metal.

6. Describe an experiment to show the reaction between chlorine and (a) sodium; (b) copper. Write equations to show the reactions.

7. Describe and explain what happens when powdered antimony is dropped into a bottle of chlorine. Write the equations to represent the reactions.

8. Using chlorine and hydrogen, describe an experiment to illustrate combustion. Write the equation.

9. (a) Using warm turpentine, describe an experiment to illustrate the great affinity of chlorine for hydrogen. (b) How could each of the products in the above reaction be identified?

10. (a) Explain with the aid of equations, the bleaching action of chlorine. (b) Explain why chlorine bleaches damp litmus paper but does not bleach dry litmus paper. (c) Compare the bleaching action of chlorine with that of sulphur dioxide. (d) Explain why chlorine water that has been left standing for some time will not bleach. Use an equation in your explanation.

11. List five commercial uses of chlorine.

12. (a) What types of materials can not be bleached with chlorine? Why? (b) When chlorine is used as a bleaching agent, what precautions are taken to prevent injury to the substances bleached?

13. Explain the action of chlorine as a germicide. Why is the chlorination of drinking water so necessary today?

14. (a) Describe how bleaching powder is made. Write the equation for the reaction. (b) How is the available chlorine liberated from bleaching powder? Write the equation.

15. What is *javelle water*? For what is it used? Explain the action.

16. Describe a good laboratory test for detecting the presence of chlorine.

17. (a) How and by whom was bromine first discovered? (b) What does the word *bromine* mean? Why is this name appropriate? (c) What are the chief commercial sources of bromine?

18. Using a diagram to illustrate your answer, describe a laboratory method for the preparation and collection of bromine. Write the equation for the reaction.

19. Describe the commercial method for the recovery of bromine from seawater.

20. List (a) ten physical properties and (b) five chemical properties of bromine.

21. Using the electron theory, explain why bromine is not as active as chlorine.

22. (a) State four commercial uses of bromine compounds. (b) Describe a good laboratory test for detecting the presence of bromine.

23. (a) What contributions were made by Courtois and Gay-Lussac to the discovery of the element iodine? (b) What was the original source of iodine? What is the modern source?

24. (a) Make a diagram of the apparatus that could be used to prepare iodine in the laboratory. (b) What property of iodine makes its method of collection different from that of chlorine? (c) Write the equation for the preparation of iodine.

25. Describe four commercial methods for obtaining iodine from natural sources.

26. (a) List (i) five physical properties and (ii) three chemical properties of iodine. (b) Using the electron theory, explain why iodine is less active than either chlorine or bromine.

27. (a) Name four uses of iodine and its compounds. (b) Describe a good laboratory test for detecting the presence of iodine. (c) Sometimes when a bandage is placed over a cut that has been treated with tincture of iodine, the bandage shows blue stains. Explain.

28. You are given three white crystalline solids one of which is a chloride, one a bromide and one an iodide. Describe how you could identify each and accompany your answer with suitable equations.

B

1. Both manganese dioxide and potassium permanganate oxidize hydrochloric acid to chlorine. What is the meaning of this statement? How many grams of each of these oxidizing agents will be required to produce 10 litres of chlorine at S.T.P.

2. What volume of chlorine measured at 18° C. and 770 mm. pressure could be obtained by the action of hydrochloric acid on 50 gm. manganese dioxide?

3. (a) What weight of bleaching powder would be required to liberate 15 litres of chlorine measured at 30° C. and 756 mm. pressure? (b) What weight of acid would be used up in the process?

4. (a) How many grams of chlorine would be required to liberate 20 grams of bromine from sodium bromide solution? (b) What volume would the chlorine occupy at S.T.P.? (c) If the bromine is recovered as liquid bromine, what volume would it occupy?

5. If 50 litres of chlorine at 100° C. and 760 mm. pressure are passed into excess of a solution of sodium bromide, what volume of bromine can be driven off if measured at the same temperature and pressure as the chlorine?

CHAPTER 22

Periodic Classification of the Elements

I consider it well to observe that no law of nature, however general, has been established all at once; its recognition is always preceded by many hints; the establishment of a law, however, does not take place when its significance is recognized, but only when it has been confirmed by experiment, which the man of science must consider as the only proof of the correctness of his conjectures and opinions.

MENDELÉEFF

Relationships between atomic weights and chemical activity were noted as early as 1817, but it was not until 1864 that John Newlands, an English chemist, published a series of papers drawing attention to the fact that "If the elements are arranged in the order of the new (atomic) weights, derived by Cannizzaro in 1858, the eighth element, starting from a given one, is a kind of repetition of the first—just like the eighth note in an octave of music." He submitted his **Law of Octaves** to the Chemical Society of London in 1866. The Chemical Society, however, because of lack of knowledge and understanding, refused recognition. Newlands, discouraged by the attitude and ridicule of some of his contemporaries, failed to pursue further research with the result that credit for presenting the first acceptable system of classification has been given to Dmitri Ivanovitch Mendeléeff, a Russian chemist (1834-1907).

Mendeléeff's classification. Mendeléeff was a careful thinker and more mature than Newlands, and he was also a chemist of considerable merit. The following paragraph from his writings expresses his mode of reasoning.

"Where it is impossible to make measurements, one is reluctantly obliged to limit oneself to approximate comparisons founded on apparent signs which are not distinct and are wanting in exactitude. But in the elements there is one accurately measurable property which is subject to no doubt, namely the property which is expressed in their atomic weights. Its magnitude indicates the relative mass of the atom . . . therefore it is most natural to seek for a dependence between the properties and analogies of the elements on the one hand and their atomic weights on the other."

Such was the concept that led Mendeléeff to arrange all of the then known elements in order of their increasing atomic weights. A periodic repetition of properties of the elements became apparent and resulted in the periodic law stating that *"If all the elements are arranged in the order of their increasing atomic weights, a periodic repetition of properties is obtained."* In 1869, Mendeléeff presented to the Russian Chemical Society a paper entitled "On the Correlation of the Properties and Atomic Weights of the Elements." His original conclusions so closely resemble those accepted today that they warrant mention here.

1. The elements, if arranged according to their atomic weights, exhibit an evident periodicity of properties.

2. Elements, similar as regards their chemical properties, have atomic weights that are either, or nearly, the same value or that increase regularly.

3. The arrangement of the elements, or of groups of elements, in the order of their atomic weights corresponds with their valences.

4. The magnitude of the atomic weight determines the character of an element.

5. The discovery of many yet unknown elements may be predicted.

6. The atomic weight of an element may sometimes be corrected by aid of a knowledge of the atomic weights of the adjacent elements.

7. Certain characteristic properties of the elements can be foretold from their atomic weights.

If the atomic weights of the elements are examined, something amiss will be noticed in connection with three sets of the elements. Argon, with an atomic weight of 39.9, precedes potassium with an atomic weight of 39.1. Cobalt, atomic weight 58.94, precedes nickel, atomic weight 58.69. Tellurium, atomic weight 127.6, precedes iodine, atomic weight 126.92.

Moseley's classification. As a result of the brilliant research accomplished by H. G. J. Moseley, a young British scientist who lost his life at Gallipoli in 1915 in the First World War, the use of atomic weights

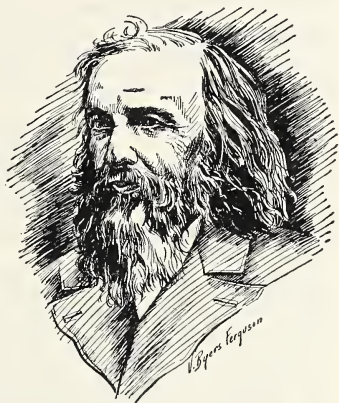


Fig. 22.1. Dmitri Ivanovitch Mendeléeff (1834-1907), originator of the first periodic classification.

as a basis for classification has been discarded in favour of **atomic numbers**. The atomic number of an element corresponds to the number of protons in the nucleus of its atom, or the number of planetary electrons. When the elements are arranged in the order of their atomic numbers, without any exception a periodicity of properties results. Hence, the **Periodic Law** is now stated as follows: *The chemical properties of the elements are periodic functions of their atomic numbers.*

A TYPICAL FAMILY

The **halogens**, chlorine, bromine and iodine, offer an excellent illustration of the arrangement of elements into groups having not only marked similarities, but also a gradation of properties as the atomic numbers increase.

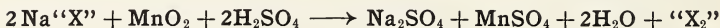
Important similarities. 1. *Atomic structure.* Each halogen atom lacks one electron in its outer orbit. Having seven valence electrons, each atom readily acquires one electron from any source in an effort to make the outer orbit complete with eight electrons (stable octet).

2. *Valence.* All exhibit a negative valence of one.

3. *Odour.* All possess a choking irritating odour.

4. *Bleaching action.* All exhibit bleaching properties, the action becoming definitely more feeble as the atomic number increases.

5. *Preparation.* All may be prepared by the same general method from the sodium or potassium halide:



6. *Reaction with metals.* All react chemically with metals producing corresponding chlorides, bromides, or iodides.

7. *Reaction with hydrogen.* All form similar hydrides (HCl, HBr, HI).

8. *Molecular formula.* All are similar in that the molecule is diatomic (Cl_2 , Br_2 , I_2).

Gradation of properties. 1. *Physical state.* At ordinary temperatures, chlorine is a gas, bromine a liquid, and iodine a solid.

2. *Colour.* Chlorine is greenish-yellow, bromine reddish-brown, and iodine steel-grey with a deep-violet vapour.

3. *Atomic number.* Chlorine 17, bromine 35, iodine 53.

4. *Atomic weight.* Chlorine 35.5, bromine 80, iodine 127.

5. *Activity.* Chemical activity decreases with increased atomic number. This is particularly true with respect to the activity with non-metals. The relative activities are also illustrated in the experiments designed to show that chlorine displaces bromine and iodine from bromides and iodides, respectively, and that bromine displaces iodine from iodides.

THE PERIODIC CLASSIFICATION

General observations. 1. The valence of the element corresponds to the number of the group in which the element occurs. (The inert gases have a valence of zero (0) since these elements do not form compounds.)

2. When hydrogen is taken as the standard, the valence of the elements increases regularly from Group I to Group IV and then decreases to Group VII.

3. When oxygen is taken as the standard, the valence increases regularly from Group I to Group VII.

4. Metallic (basic) elements occur on the left and non-metallic (acidic) elements occur on the right.

5. Metallic characteristics increase from top to bottom in any given group.

6. The members of a group resemble one another, but the members of a family in the group are more closely related.

7. A study of one typical member of each group furnishes much information about the other members.

8. A move in any direction from francium (No. 87), results in a decrease in the metallic nature of the elements.

9. A move in any direction from fluorine (No. 9) results in an increase in metallic characteristics.

Importance. The periodic classification of the elements greatly simplified the study of their physical and chemical properties. In addition, the discovery of new elements, as predicted by Mendeléeff, was made possible. The element now called *germanium* (named *eka-silicon* by Mendeléeff) is an example of the close relation between prediction and fact.

<i>Predicted Properties</i>		<i>Confirmed Properties</i>	
atomic weight	72	atomic weight	72.6
specific gravity	5.5	specific gravity	5.46
oxide, EsO_2 , s.g.	4.7	oxide, GeO_2 , s.g.	4.7
valence	4	valence	4

Another important role played by the system brought about the correction of the atomic weights of certain elements. Before the classification was made, the discrepancies were not so noticeable, but when the elements became associated in groups individual differences were more evident.

Imperfections in the Periodic Classification. There are several defects in the present periodic classification and many attempts have been made to revise it.

THE PERIODIC TABLE OF THE ELEMENTS

TYPE OF HYDRIDE	RH	RH ₂	RH ₃	RH ₄	RH ₅	RH ₆	RH ₇	RH ₈	RH	RO ₄
TYPE OF OXIDE	R ₂ O	RO	RO ₂	RO ₃	RO ₄	RO ₅	RO ₆	RO ₇	R ₂ O ₇	RO ₄
PERIOD	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII		
1	1 Hydrogen 1.008									
2	3 Lithium 6.940	4 Beryllium 9.013	5 Boron 10.82	6 Carbon 12.01	7 Nitrogen 14.008	8 Oxygen 16.000	9 Fluorine 19.00			
3	11 Sodium 22.997	12 Magnesium 24.32	13 Aluminum 26.97	14 Silicon 28.06	15 Phosphorus 30.98	16 Sulphur 32.066	17 Chlorine 35.457			
4	19 Potassium 39.096 29 Copper 63.54	20 Calcium 40.08 30 Zinc 65.38	21 Scandium 45.10 31 Gallium 69.72	22 Titanium 47.90 32 Germanium 72.60	23 Vanadium 50.95 33 Arsenic 74.91	24 Chromium 52.01 34 Selenium 78.96	25 Manganese 54.93 35 Bromine 79.916	26 Iron 55.85 27 Cobalt 58.94 28 Nickel 58.69		
5	37 Rubidium 85.48 47 Silver 107.88	38 Strontium 87.63 48 Cadmium 112.41	39 Yttrium 88.92 49 Indium 114.76	40 Zirconium 91.22 50 Tin 118.70	41 Columbium 92.91 51 Antimony 121.76	42 Molybdenum 95.95 52 Tellurium 127.61	43 Technetium 99.00 53 Iodine 126.92	44 Ruthenium 101.7 45 Rhodium 102.91 46 Palladium 106.7		
6	55 Cesium 132.91 79 Gold 197.2	56 Barium 137.36 80 Mercury 200.61	57* Lanthanum 138.92 81 Thallium 204.39	72 Hafnium 178.6 82 Lead 207.21	73 Tantalum 180.88 83 Bismuth 209.0	74 Tungsten 183.92 84 Polonium 210.0	75 Rhenium 186.31 85 Astatine 211.0	76 Osmium 190.2 77 Iridium 193.1 78 Platinum 195.23		
7	87 Francium 223.0 97 Berkelium 243.0	88 Radium 226.05 98 Californium 244.0	89 Actinium 227	90 Thorium 232.12	91 Protactinium 231.0	92 Uranium 238.07	93 Neptunium 237.0	94 Plutonium 239.0 95 Americium 241.0 96 Curium 242.0		

*Following Lanthanum are 14 elements known as The Rare Earths

1. Hydrogen does not fit into any group. It is placed in Group I, because its chemical properties and electron configuration most closely resemble the elements of this group.

2. Elements with variable valence have family relations in more than one group.

3. Chemically related elements such as copper and mercury are separated by the table.

In spite of these discrepancies, the periodic arrangement is apparently based on some fundamental relationship, and with further research it is quite possible that all irregularities will be eliminated.

EXERCISE

1. State the Law of Octaves. Who submitted this law, and why was it refused recognition?

2. (a) State the Periodic Law as advanced by Mendeléeff. (b) What were the seven original conclusions made by Mendeléeff? (c) What discrepancies became apparent in Mendeléeff's arrangement?

3. (a) State the Periodic Law as advanced by Moseley. (b) What improvement was brought about by Moseley's classification?

4. List eight important similarities of the halogens.

5. Show how the gradation of properties of chlorine, bromine and iodine can be illustrated by the following: (a) physical state; (b) colour; (c) atomic number; (d) atomic weight; (e) activity.

6. In the Periodic Classification, how is (a) valence related to group number; (b) group valence related to hydrogen valence; (c) group valence related to oxygen valence?

7. Using diagrams, show how the atomic structure of (a) sodium and (b) chlorine is related to group number and valence.

8. Where in general do the (a) metallic and (b) non-metallic elements occur in the Periodic Classification?

9. Give two contributions to the advancement of chemistry made by the adoption of the Periodic Classification.

10. State three problems that still remain unsolved in the Periodic Classification of the elements.

CHAPTER 23

The Alkali Metals

After I had detected the bases of the fixed alkalies (i.e. the elements sodium and potassium), I had considerable difficulty to preserve and confine them so as to examine their properties and submit them to experiments; for like the *alkahests* imagined by the alchemists, they acted more or less upon almost every body to which they were exposed.

SIR HUMPHRY DAVY

The members of family A of Group I in the Periodic Classification are the most active of all the metallic elements. The alkali metals will decompose water at ordinary temperatures, form soluble oxides and hydroxides which act as strong bases, and produce many salts, all of which are soluble. An atom of each alkali metal has one electron in the valence ring, and, because this single electron can be easily "loaned", the alkali metals are very active.

Following is a list of the alkali metals with some of their properties.

SOME PROPERTIES OF ALKALI METALS

ELEMENT	ATOMIC WEIGHT	VALENCE	SPECIFIC GRAVITY	MELTING POINT	RING STRUCTURE
Lithium	6.94	1	.53	186° C.	2, 1
Sodium	23.00	1	.97	97.5° C.	2, 8, 1
Potassium	39.10	1	.86	62.3° C.	2, 8, 8, 1
Rubidium	85.48	1	1.53	38.5° C.	2, 8, 18, 8, 1
Cesium	132.90	1	1.9	28.5° C.	2, 8, 18, 18, 8, 1
Francium	223.00	1			2, 8, 18, 32, 18, 8, 1

SODIUM

Occurrence. Because of the great activity of sodium, it is never found free in nature, but always in chemical combination. The most common source of sodium is common salt (Chapter 20). Other naturally occurring compounds containing sodium are, sodium nitrate (NaNO_3), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$), and cryolite (Na_3AlF_6).

Preparation. Sodium is prepared by the electrolysis of either fused sodium chloride or fused sodium hydroxide. These substances, when fused, are good conductors of electricity, and because no water is present the sodium produced can be easily collected if air is excluded from the receiver.

In the **Downs process**, a direct current of electricity, passed through fused sodium chloride, causes chlorine to be liberated at a central carbon anode, while the sodium collects at a ring-shaped cathode surrounding the anode. The chlorine collects in a specially designed compartment above the anode, and the sodium, being lighter than the fused salt rises and overflows into a separate container.

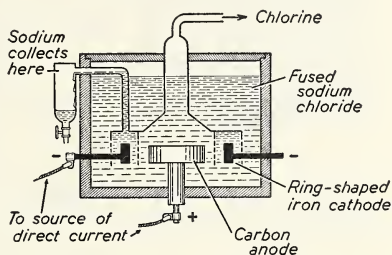
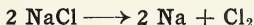
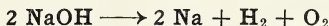


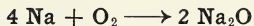
Fig. 23.1. A Downs cell. The products of electrolysis of fused sodium chloride are sodium and chlorine.



In the **Castner process**, a direct current of electricity is passed through fused caustic soda in an iron container. The sodium is attracted to an iron cathode, situated in the centre of the cell. Globules of sodium, and hydrogen gas, rise and collect in a bell-shaped vessel of iron. The hydrogen serves to keep air away from the sodium. Oxygen, liberated at a nickel-iron anode surrounding the cathode, escapes through an opening in the lid of the container.



Properties. Sodium is a soft, silvery-white solid. It melts at 97.5°C . to form a silvery liquid. It tarnishes quickly in air, and when ignited burns vigorously with a yellow flame forming a mixture of its two oxides.



It combines directly with the halogens forming the corresponding halides (NaCl , NaBr , NaI). Sodium reacts vigorously with water, forming sodium hydroxide and hydrogen.



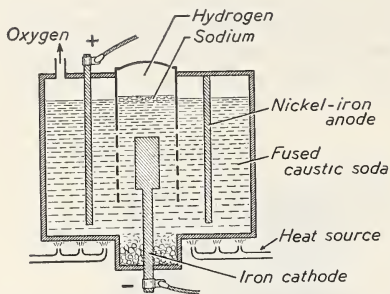


Fig. 23.2. A Castner cell. The products of electrolysis of fused sodium hydroxide are sodium, hydrogen, and oxygen.

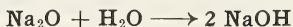
Because of its vigorous action with oxygen and water, sodium is stored in kerosene or other oils with which it is inactive.

Uses. Metallic sodium has little practical use. It is the direct source of a limited number of important compounds (e.g. sodium peroxide), and sodium-vapour lamps are gaining in importance for highway illumination.

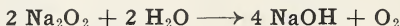
Test. Sodium vapour imparts a characteristic yellow colour to the non-luminous flame of burning hydrogen. This same yellow colour is produced whenever any sodium compound is volatilized in a non-luminous flame. Hence if a clean piece of platinum wire is dipped into a concentrated solution of any sodium compound and held in a non-luminous flame, a *yellow* colour will be observed.

SODIUM COMPOUNDS

Sodium oxide (Na_2O) is formed by the slow oxidation of sodium in a limited current of air at temperatures between 200°C . and 400°C . It is a white amorphous mass which reacts violently with water to form sodium hydroxide.



Sodium peroxide (Na_2O_2) is formed when sodium burns in excess of air or oxygen. It is a yellow solid which, on standing exposed to air, turns white because of the formation of sodium hydroxide and finally sodium carbonate. When water is added to sodium peroxide, the solution becomes strongly alkaline and there is a rapid evolution of oxygen gas.



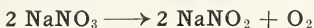
Sodium chloride is of such great importance that a separate chapter (Chapter 20) has been assigned to its study.

Sodium carbonate is one of the most important sodium compounds. Its preparation from sodium chloride by the Solvay, or ammonia-soda, process constitutes a major chemical industry. It is soluble in water, giving a strongly alkaline solution. The decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$,

commonly known as washing soda, is used on a large scale in the softening of water, and for the manufacture of glass, soap, textiles, baking soda, and caustic soda.

Sodium bicarbonate is also produced by the Solvay process, and is soluble in water, giving a mild alkaline solution. It is used medicinally to correct excess stomach acidity, and in baking as baking soda, or as one of the components of baking powder.

Sodium nitrate, or Chile saltpetre, is more important as a compound of nitrogen than as a sodium compound. It liberates oxygen readily when heated, but it is not satisfactory for use in gunpowder because it is hygroscopic.



It is used in considerable quantities as a fertilizer, in the manufacture of nitric acid, and in the preparation of ordinary saltpetre.

Sodium hydroxide is in great demand in industry because of its versatility and low price. It is prepared by the electrolysis of brine. It is a white, brittle, deliquescent solid which produces a very strong base in solution. A commercial product, containing about 24% water, is known as caustic soda and has a very corrosive action on organic matter and many other substances. A water solution of sodium hydroxide, sometimes designated as soda lye or lye, has a soapy feel, a bitter taste, is a good conductor of electricity and dissolves grease and other matter of plant and animal origin. Sodium hydroxide is used in the manufacture of soap, rayon, textiles, petroleum products, and many other chemicals. Since it is deliquescent, it is used to remove *moisture* from gases, and, because it reacts with carbon dioxide to form sodium carbonate, it is also used to remove *carbon dioxide* from air (e.g. in submarines and in basal metabolism tests).

Sodium silicate (Na_2SiO_3) is very soluble in water, and a concentrated solution is sold under the name of "water glass". This commodity preserves eggs, and it also serves as a filler in some soaps, as a coating to fireproof wood and textiles, and as an adhesive cement for glass and porcelain.

Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$) (hypo), forms white, translucent, well-defined hexagonal crystals. It has a tendency to remain indefinitely in a state of supersaturation, and for this reason is a valuable compound in the laboratory study of supersaturated solutions. In industry, it is used extensively as an *antichlor* in the removal of the last traces of chlorine from bleached fabrics. Because it dissolves silver salts, it is employed as a "fixer" in photography.

POTASSIUM

Occurrence. Potassium is an essential constituent of the minerals feldspar and mica, and is widely distributed in rocks, soil, and saline residues from former inland lakes. The most important deposits of potassium compounds are found at Stassfurt, Germany; Alsace; Poland; Searles Lake in California; and in an area of about 50,000 square miles in New Mexico and Texas. In each of these deposits, potassium chloride is the most plentiful and also the most important compound.

Preparation. Potassium is prepared by the electrolysis of fused potassium chloride or potassium hydroxide by the same methods as are used for sodium.

Properties. Potassium is a soft, silvery-blue solid. Because of its vigorous action with oxygen and water, it is stored in kerosene or other oils. When placed on water, the reaction produces enough heat to cause the liberated hydrogen to burn.

Uses. Other than being an interesting element to study in the laboratory, potassium has few uses. Certain of its salts, however, are very valuable as fertilizers and explosives.

Test. Potassium vapour imparts a violet colour to a non-luminous flame. A clean piece of platinum wire, dipped into a concentrated solution of any potassium compound and held in a non-luminous flame, will give a characteristic *violet* colour.

POTASSIUM COMPOUNDS

Most potassium compounds are so similar to their sodium counterparts that little space will be given to their study.

Potassium hydroxide, or caustic potash, is manufactured by methods similar to those outlined for sodium hydroxide. It is used in making "soft" and "liquid" soaps.

Potassium chloride, with properties similar to those of sodium chloride, is used extensively as a source of other potassium compounds and as a fertilizer. Commercial fertilizers show the importance of the elements nitrogen, phosphorus, and potassium ("N-P-K") being sold on a percentage basis content. For example, a 3-9-5 fertilizer contains 3% available nitrogen, 9% available phosphorus, and 5% available potassium.

Potassium nitrate, known as saltpetre, or nitre, is described earlier.

Potassium chlorate is a good oxidizing agent and is used in the laboratory preparation of oxygen. It is used in the manufacture of fireworks, matches, and explosives because it readily decomposes to

liberate oxygen. It is also contained in mouthwashes, gargles, and tooth pastes.

Potassium permanganate (KMnO_4), because of its oxidizing properties, is used medicinally both as a disinfectant and a deodorant. It bleaches resins, fats, waxes, oils, straw, cotton, silk, and chamois skins. It is sometimes employed as a remedy for victims of poison ivy.

EXERCISE

A

1. Sodium and potassium are members of the same chemical family. Give five properties of these two elements to show that there is a marked similarity in their chemical behaviour.

2. Why would you not expect to find any of the alkali metals occurring free in nature?

3. List with their formulae four naturally occurring compounds of sodium. Which of these is the most important? Why?

4. (a) Compare the Downs and Castner processes for making metallic sodium under the following headings: (i) energy used; (ii) type of apparatus used; (iii) by-products; (iv) usefulness of by-products. (b) Write equations for each of the processes mentioned in (a).

5. (a) List (i) four physical and (ii) five chemical properties of sodium. (b) Since sodium has a specific gravity of 0.97, one would expect it to float on water at least nine-tenths submerged. However, observation shows that only about one-tenth is submerged. Explain.

6. (a) Give at least six observations noticed when a small piece of sodium is dropped on water. (b) Why are both sodium and potassium stored in kerosene?

7. Write equations for (a) the burning of sodium in air and (b) the action of sodium on water.

8. Tabulate the commercial source, formula, and important uses of each of the following: common salt, sodium oxide, sodium peroxide, sodium carbonate, sodium bicarbonate, sodium nitrate and sodium hydroxide.

9. Potassium occurs as a constituent of both feldspar and mica. Canada has huge deposits of these minerals, yet Canada has to import practically all the potassium salts used industrially. Can you suggest a reason for this?

10. Compare sodium and potassium with respect to (a) method of preparation; (b) colour; (c) hardness; (d) density; (e) method of storage; (f) action on water; (g) uses; (h) their salts; (i) test for the element or any of its compounds.

11. (a) Describe how potassium hydroxide is made. What by-products are produced? Write equations to illustrate the various chemical reactions that occur during the process.

12. Why is potassium nitrate a more valuable fertilizer than sodium nitrate?

13. Why is potassium permanganate a good disinfectant?

14. Write the chemical name and the formula for each of the following: saltpetre, baking soda, Chile saltpetre, common salt, caustic potash, caustic soda, "hypo", and washing soda.

15. At the beginning of this chapter, there is a table showing a few of the characteristics of the seven metals that are known as alkali metals. These metals **increase** in activity from lithium to francium. Using the electron theory, explain

(a) why francium is the most active metal and (b) why potassium is more active than sodium.

16. It is not likely that you have ever seen a sample of rubidium. From your study of the properties of sodium and potassium and from the position of rubidium in the Periodic Table, what do you think would be the physical and chemical properties of rubidium? (Make comparisons with sodium and potassium.)

B

1. Which will liberate more carbon dioxide by the use of sulphuric acid, 100 gm. washing soda crystals or 70 gm. baking soda?

2. If 20 pounds of molten caustic soda were used up by electrolysis in a Castner cell, what weight of metallic sodium would be produced?

3. (a) A solution containing 40 gm. potassium hydroxide was neutralized with sulphuric acid solution. What weight of sulphuric acid was used? (b) If the acid solution used in (a) occupied 200 cc., what was the concentration of the solution in grams of acid per litre of solution?

CHAPTER 24

Compounds of Nitrogen

... The fixation of nitrogen is vital to the progress of civilized humanity, and unless we can class it among the certainties to come, the great Caucasian race will cease to be the foremost in the world, and will be squeezed out by the races to whom wheaten bread is not the staff of life.

SIR WILLIAM CROOKES

Nitrogen does not react readily with any of the elements. Therefore, although 78 per cent of the atmosphere is nitrogen, there are few of its mineral compounds on earth. However, many organic compounds, containing nitrogen, are built up by plants which utilize the products of the life activities of nitrogen-fixing bacteria in the soil, the carbohydrates manufactured in their leaves, and soil minerals. These

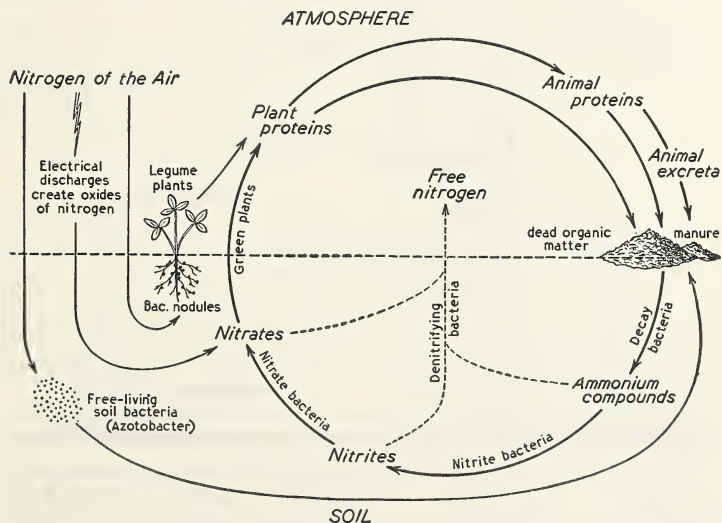


Fig. 24.1. The nitrogen cycle. The chain of events that maintains a balance between the nitrogen of the air and all living things.

complex organic compounds, containing nitrogen, are called **proteins**. Animals eat plant proteins, and by the processes of digestion and absorption, as well as by other chemical changes, rearrange the atoms into animal proteins such as are found in blood, bone, and muscle. Foods, supplying much of our proteins, are lean meats, nuts, peas, beans, cheese, eggs, and milk. From the waste products of animals and plants, and from the decay, or decomposition of their remains nitrogen is returned to the air. This nitrogen may again be "fixed" in the form of some simple nitrogen compound by the action of bacteria and again be made available for the higher plants. This chain of events maintains the balance between nitrogen in the air and living things, and is called the **nitrogen cycle**.

Man has also devised methods of fixing free nitrogen. Nitrogen fixation is accomplished in industry in two different ways, depending on whether atmospheric nitrogen is made to combine with hydrogen to form ammonia, or with oxygen to form nitric oxide. A discussion of these syntheses follows.

AMMONIA (NH_3)

The alchemists called a solution of ammonia in water "spirits of

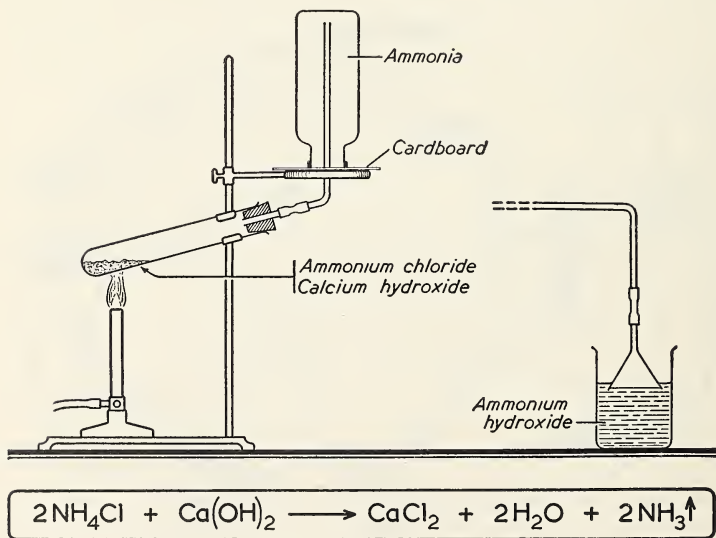


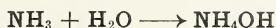
Fig. 24.2. The laboratory preparation and collection of ammonia. Ammonium hydroxide solution may be prepared by passing ammonia into water as shown.

hartshorn" because they obtained it by heating the horns of deer. The pure gas, however, was not collected and identified until Priestley, by means of his pneumatic trough, collected it over mercury in 1774.

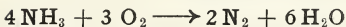
Occurrence. Because ammonia is a product of the decay of organic matter containing nitrogen, traces of it are found in the air, and traces of ammonia solution are present in most natural waters.

Preparation. Ammonia can be prepared in the laboratory by heating any ammonium compound with any base. Usually ammonium chloride and slaked lime are used (Fig. 24.2).

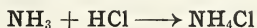
Properties. Ammonia is a colourless gas with a characteristic, pungent odour. It can be easily liquefied and is less dense than air (17:28.9). It is soluble in water, one volume of water at 0° C. and standard pressure dissolving 1,298 volumes of the gas to give a solution containing 47% of ammonia by weight. This extreme solubility of ammonia is caused by the reaction between the gas and water, whereby ammonium hydroxide, a weak base, results.



Ammonia does not burn in air nor does it support combustion. It burns slowly in pure oxygen.



Ammonia reacts with hydrogen chloride to form dense white clouds of ammonium chloride (sal ammoniac).



Industrial preparation. 1. *Gas-works ammonia.* During the destructive distillation of coal, an alkaline liquid, known as "gas liquor", is formed. This contains ammonium salts and free ammonia and, when heated with slaked lime, yields ammonia gas, which can be either dissolved in water or passed into sulphuric or hydrochloric acids to form ammonium sulphate or ammonium chloride.

2. *Synthetic ammonia.* Large quantities of ammonia are prepared by the direct union of nitrogen and hydrogen.

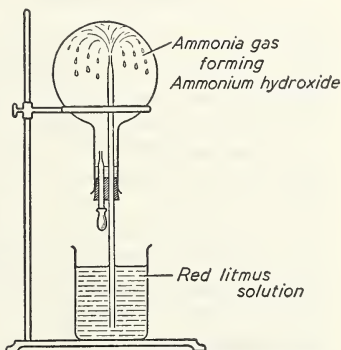
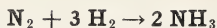
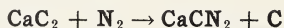


Fig. 24.3. Ammonia fountain. Ammonia is so soluble that when a few drops of water are forced by a dropper into a flask filled with the gas, the ammonia dissolves so rapidly that it creates a partial vacuum in the flask. Air pressure forces the red litmus solution up the tube to form a "blue" fountain.

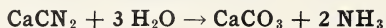


The nitrogen is obtained by the fractional distillation of liquid air, and the hydrogen usually from the electrolysis of brine. This industrial preparation was perfected by a German chemist, Fritz Haber. In the **Haber process**, a mixture of nitrogen and hydrogen, under a pressure of 200 atmospheres, is passed through steel tubes electrically heated to 500° C. Finely divided iron or iron oxide is used as a catalyst. The resulting ammonia is dissolved in water.

3. *Cyanamide process.* If calcium carbide is heated electrically for about 48 hours while nitrogen under pressure is passed over it, calcium cyanamide and carbon are formed.



Although most of the cyanamide is used directly as a fertilizer, some of it is used in the preparation of ammonia. To do this, calcium cyanamide is mixed in autoclaves with water and sodium hydroxide, and steam under pressure is blown in.



Uses. Ammonia is used in the manufacture of washing soda by the Solvay process, and in the production of nitric acid and nitrates, and the subsequent manufacture of explosives.

Because it can be so easily liquefied, and because of its high heat of vaporization (326 cal. per gm.), ammonia is used in refrigeration. The gas is first condensed under pressure and the rapid evaporation of the liquid, resulting from the sudden release of pressure, causes an absorption of heat whereby the surrounding area is cooled.

An aqueous solution of ammonia, called household ammonia, contains about 6% ammonia gas by weight, and is used in the laundry and for household cleaning.

Ammonium compounds are prepared either by the direct union of ammonia with acids or by the neutralization of ammonium hydroxide solution. They all contain the radical NH_4 which behaves like a metal in chemical reactions. All ammonium salts are soluble in water and all are easily decomposed by heat. Ammonium carbonate has largely replaced the aqueous solution of ammonia as a household cleaning agent because it is easier to handle and yields ammonia readily. The carbonate is also used in smelling salts. Ammonium chloride (sal ammoniac) is used in dry cells, the nitrate of ammonium in making explosives, and the sulphate as a fertilizer.

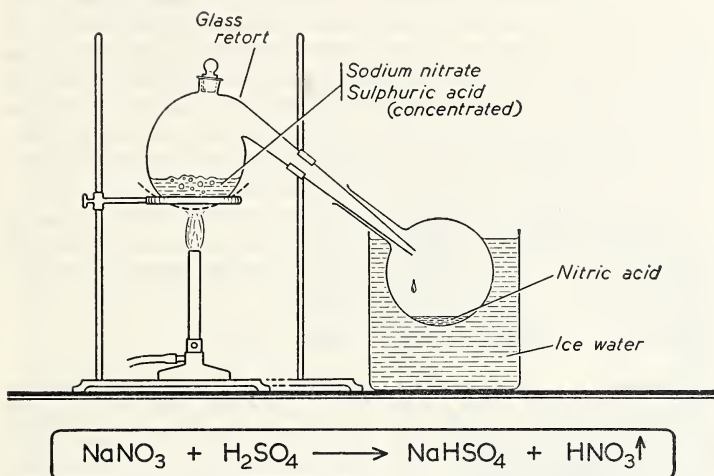


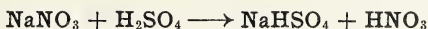
Fig. 24.4. The laboratory preparation and collection of nitric acid.

NITRIC ACID (HNO_3)

Nitric acid was known to the alchemists as *aqua fortis* (strong water). They obtained it by heating together saltpetre and some hydrated sulphate such as green vitriol ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$).

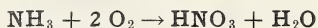
Preparation. There are three important methods used in the preparation of nitric acid.

1. *From Chile saltpetre.* In the laboratory, nitric acid is prepared by heating a nitrate with concentrated sulphuric acid. Chile saltpetre (sodium nitrate) is commonly used because it is the cheapest of all the nitrates. When concentrated sulphuric acid and sodium nitrate are placed in the retort (Fig. 24.4), no reaction takes place, but if the mixture is gently heated, effervescence in the liquid is observed. Nitric acid boils at 86°C . and sulphuric acid at 338°C ., so that while the nitric acid vapour is driven off and condensed, the temperature is not high enough to vaporize the sulphuric acid. Because nitric acid attacks both rubber and cork, the retort must be equipped with a glass stopper. This method, employing larger retorts and special condensers, is that used industrially. The residue in the retort crystallizes to form sodium bisulphate.



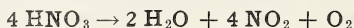
2. *By the oxidation of nitrogen at high temperatures.* When air is heated to 3500°C ., about 5% of it is converted into a gas called nitric oxide. This combination of two of the components of air is a true nitrogen fixation. The resulting cooled nitric oxide oxidizes in more air to form nitrogen dioxide, and this is dissolved in water to form nitric acid. This process, however, is so wasteful of electrical energy that, even in places where electricity is very cheap, it is being displaced by the more economical oxidation of synthetic ammonia.

3. *By the oxidation of ammonia (Ostwald Process).* In the presence of a suitable catalyst (usually red-hot platinum), ammonia and oxygen react to form nitric acid and water. The reactions, although complex, may be represented by one simple equation:

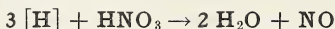


Properties. The acid solution is colourless; the yellow colour so often seen is caused by the liberation of nitrogen dioxide. Commercial concentrated nitric acid contains about 68% HNO_3 . If a drop of such acid is placed in 10 cc. of water, the dilute solution will have a sour taste, turn blue litmus red, neutralize a base, and show most of the other characteristics of an acid solution. Nitric acid ionizes to a high degree and is therefore, a strong acid. In addition, the concentrated acid is very corrosive to flesh and clothing.

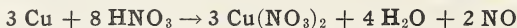
Nitric acid is not very stable. When heated or exposed to sunlight, it decomposes to form water, nitrogen dioxide, and oxygen. Hence, nitric acid, particularly when hot, is an excellent oxidizing agent.



This oxidizing property explains its peculiar reaction with metals. With zinc and other metals above hydrogen in the activity series, and dilute acid, one would expect to get hydrogen; however, water and not hydrogen is obtained. This is because of the strong oxidizing property of the nitric acid. Any hydrogen atoms set free are immediately oxidized to water.



With copper and dilute nitric acid, the reaction is similar to that with zinc.



With concentrated acid, nitrogen dioxide (NO_2) is formed.



Nitric acid does not act on either platinum or gold.

Nitric acid will also oxidize non-metals such as sulphur and carbon to form sulphuric acid and carbon dioxide, respectively. It also acts as a powerful oxidizer with proteins, including skin, which it turns a yellow colour. The addition of ammonium hydroxide intensifies the yellow colour to orange. These reactions are used as a test for proteins.

Uses. By far the most important use of nitric acid is in the manufacture of explosives. Other uses include the preparation of dyes, drugs, photographic films, fertilizers, and some plastics. It is also used to etch zinc and copper plates in preparing "cuts" to print artists' illustrations (such as Fig. 24.5).

Explosions are caused by the sudden formation and expansion of huge volumes of gases. Violent explosions occur when solids or liquids suddenly change into gases of several hundred times their volume. Heat formed from these exothermic reactions causes the liberated gases to expand still more. The most important explosive used today was discovered by Antonio Sobrero, an Italian. It is glyceryl trinitrate, commonly known as **nitroglycerine**, and made by heating nitric acid with glycerine, a by-product of the soap industry.

This pale, oily liquid was too sensitive to be used indiscriminately for large-scale blasting until Alfred Nobel found that, by absorbing it in a porous material, it was rendered relatively safe. This product is called **dynamite**. Dynamite and other explosives have greatly altered our mode of living. An endless list could be compiled of the peacetime benefits brought to the world by the varying uses of explosives. In no country can this be better demonstrated than in Canada. Mining, one of our most important industries, makes the greatest use of explosives and employs many specialized types. Approximately 30,000 blasts are set off every day in Canadian mines. In the fishing industry, many tons of explosives are used annually for breaking ice so that sealing and whaling ships may reach their hunting grounds. In the



E. I. du Pont de Nemours

Fig. 24.5 Alfred Nobel (1833-1896), a Swedish chemist, perfected dynamite in 1867. He was the founder of the five Nobel prizes, awarded annually for the most outstanding work in physics, chemistry, medicine, literature, and for the promotion of world peace.

lumbering industry, explosives clear the rights-of-way, blow out stumps, and break up log jams. The farmer employs explosives to



Fig. 24.6. Blasting with dynamite.

C.I.L.

clear the land of stumps, and to open drainage ditches. In the city, explosives are sometimes useful in wrecking buildings, uprooting concrete foundations, felling old chimneys, and excavating for large foundations. Canada's great railways, with their thousands of rock cuts and tunnels, could not have been built without the use of explosives.

Most of our modern explosives are manufactured by treating some organic compound with nitric acid. In addition to nitroglycerine, these include cellulose nitrate (gun cotton), cordite, picric acid, mercuric fulminate, lyddite, and trinitrotoluene (T.N.T.).

Nitrates. Nitrates are made by the action of nitric acid on a metal, a metal oxide, an hydroxide, or a carbonate. They are all soluble in water and, when heated, lose oxygen to become nitrites. The most important nitrates are those of ammonium, sodium, potassium, and silver. **Sodium nitrate** (NaNO_3), sometimes called Chile saltpetre, or cubic nitrate, because it crystallizes in cubes, is found in its natural state in desert regions,

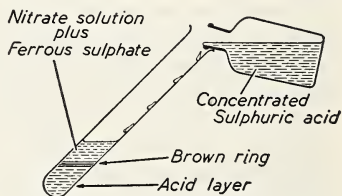
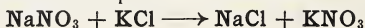


Fig. 24.7. The brown-ring test for a nitrate (nitrate ion). The ferrous sulphate solution must be freshly prepared.

particularly in Chile. It is a deliquescent salt, and is used in the preparation of nitric acid and as a fertilizer. **Potassium nitrate** (KNO_3), nitre, or saltpetre, crystallizes in long needle-like crystals. It is formed by the decay of organic matter, and appears on manure and other refuse as a white crystal salt. Saltpetre is still manufactured by this method in India and Sweden. However, the chief source today lies in the reaction of a solution of hot concentrated Chile saltpetre with a hot concentrated solution of potassium chloride.



The separation of these soluble salts is accomplished by taking advantage of their differences in solubility (see Solubility Curve p. 77). Saltpetre is used for preserving meats and, because it is not deliquescent, for the manufacture of gunpowder. Gunpowder is a mixture of saltpetre, sulphur, and charcoal.

Silver nitrate. (AgNO_3), known to the alchemists as "lunar caustic" is used in making photographic plates and films. It can be cast into sticks and used by medical doctors to "burn away" small growths or proud flesh.

Test for nitrates. The substance to be tested is dissolved in as little water as possible in a test-tube. A freshly prepared solution of ferrous sulphate is added, and concentrated sulphuric acid is poured down the side of the sloping test-tube so that it will form a bottom layer. If the original substance is a nitrate, a *brown ring* will form in the zone between the two layers (Fig. 24.7).

OXIDES OF NITROGEN

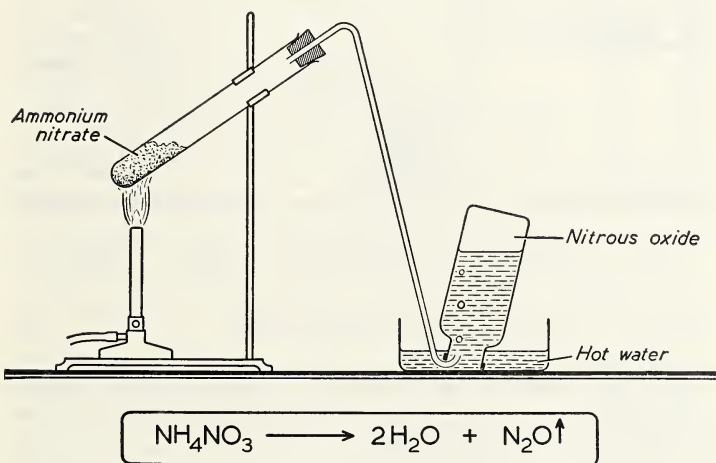


Fig. 24.8 The laboratory preparation and collection of nitrous oxide (laughing gas).

Nitrous oxide, or laughing gas (N_2O). Nitrous oxide can be prepared by heating ammonium nitrate; nitrous oxide and water are formed (Fig. 24.8). As the reaction is exothermic, the heating must be done carefully because too high a temperature may result in an explosion.

Nitrous oxide is a colourless gas with a slightly sweet odour and taste. It is denser than air (44: 28.9), and moderately soluble in water. It is generally collected over hot water. It supports the combustion of most substances almost as well as does oxygen, from which it can be distinguished by its lack of reaction with a mixture of solutions of pyrogallic acid and potassium hydroxide. Another distinguishing test is its lack of reaction with nitric oxide, a gas that reacts with oxygen to form a brown gas, nitrogen dioxide (see below).

Nitrous oxide is used as an anaesthetic in minor dental and surgical operations.

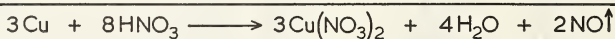
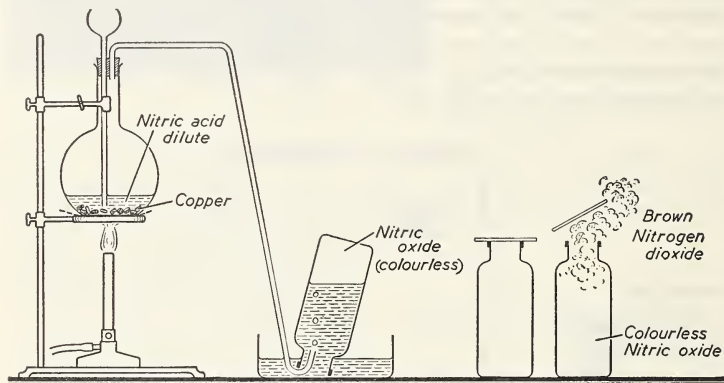
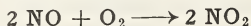


Fig. 24.9. The laboratory preparation and collection of nitric oxide. When nitric oxide is exposed to air it changes to nitrogen dioxide.

Nitric oxide (NO) is prepared in the laboratory by the action of dilute nitric acid on copper. The mixture is gently heated and the gas collected over water (Fig. 24.9).

Nitric oxide is a colourless gas, slightly denser than air (30: 28.9), and is almost insoluble in water. It does not support combustion. It is not possible to smell or taste this gas because it instantly unites with atmospheric oxygen to form nitrogen dioxide.



Nitrogen dioxide (NO₂) is formed as soon as nitric oxide is exposed to air, as indicated in the above equation. The usual laboratory method

of preparation is by the action of concentrated nitric acid on copper.

Nitrogen dioxide is a reddish-brown gas with a pungent odour. It is denser than air (46: 28.9), very soluble in water, and very poisonous. It does not burn, nor does it support combustion since it quickly extinguishes a burning splint.

EXERCISE

A

1. (a) Why is nitrogen found as a constituent of only a few minerals? (b) What is the name given to complex organic compounds that contain nitrogen? (c) What is meant by the nitrogen cycle? Explain, using a suitable diagram to illustrate your answer.

2. What two elements are made to combine with free nitrogen in industrial nitrogen fixation? Name the product formed in each case.

3. Describe a laboratory method of preparing and collecting ammonia gas. Make a diagram of the apparatus used and write the equation for the reaction.

4. Explain the action of an ammonia fountain, using a diagram to illustrate your answer.

5. Ammonia is dissolved in water in one test-tube and hydrogen chloride is dissolved in water in another. (a) State two characteristic properties of each solution. (b) What kind of substance is formed when the two solutions are mixed? Write the equation.

6. Many gases can be dried by bubbling them through concentrated sulphuric acid. Can ammonia be dried by this method? Explain.

7. Describe (a) the Haber process and (b) the cyanamide process for making ammonia. Illustrate your answer in each case with equations.

8. What are the two important physical properties of ammonia that make it useful as a refrigerant?

9. (a) Write an equation for the neutralization of ammonium hydroxide with each of the following acids: (i) sulphuric; (ii) hydrochloric; (iii) nitric; (iv) carbonic. (b) Write the name of the salt formed in each reaction in (a).

10. (a) What are three important methods used in the preparation of nitric acid? (b) Which of the three methods named in (a) is used in the laboratory? Why are the other two methods not used in the laboratory?

11. Describe in detail the laboratory method for preparing and collecting nitric acid. Make a diagram of the apparatus used and give the equation.

12. In the laboratory preparation of nitric acid, explain each of the following: (a) Why is sulphuric rather than some other acid used? (b) Why is the apparatus made entirely of glass? (c) Why is the nitric acid collected often yellowish in colour?

13. (a) Why should nitric acid be handled with extreme care? (b) Why is nitric acid regarded as a strong acid?

14. Nitric acid has a peculiar reaction with metals. To what property of the acid is this due? Illustrate with equations showing the reaction of dilute nitric acid with (a) zinc and (b) copper.

15. Write equations for the reaction of hot concentrated nitric acid on (a) copper and (b) sulphur.

16. Give the characteristic test for nitric acid.

17. (a) List five uses of nitric acid. (b) List seven explosives that are manufactured by treating organic compounds with nitric acid.

18. (a) How is nitroglycerine converted into dynamite? (b) Write an account of the importance of explosives in the development of Canada.

19. (a) Give two properties common to all nitrates. (b) Write the formula and give two uses for each of the following nitrates: sodium nitrate; potassium nitrate; silver nitrate.

20. Describe a test for the nitrate ion.

21. Describe with the aid of a diagram a laboratory method for preparing and collecting nitrous oxide. Write the equation.

22. (a) List (i) four physical properties and (ii) one chemical property of nitrous oxide. (b) A glowing splint will rekindle in both oxygen and nitrous oxide. What test could be used to distinguish between these two gases? (c) Give a use of nitrous oxide.

23. (a) Write the equation for the laboratory preparation of nitric oxide. (b) Why is nitric oxide always collected over water and never by the upward displacement of air? (c) List four properties of nitric oxide.

24. (a) Write the equation for the laboratory preparation of nitrogen dioxide. (b) List (i) four physical and (ii) three chemical properties of nitrogen dioxide.

25. Give the chemical name and formula for each of the following: saltpetre, Chile saltpetre, aqua fortis, laughing gas, lunar caustic and sal ammoniac.

B

1. (a) From the formula of ammonia gas, calculate (i) the percentage by weight of nitrogen in the compound and (ii) the weight of 10 litres of the gas at 0°C . and 760 mm. pressure. (b) In what proportion by volume does ammonia combine with hydrogen chloride to form sal ammoniac?

2. What volume of ammonia gas at S.T.P. will be needed in the preparation of 8 grams of ammonium nitrate?

3. How many litres of ammonia gas measured at 10°C . and 740 mm. pressure could be prepared from the reaction of 100 gm. ammonium chloride with excess calcium hydroxide?

4. How many pounds of nitric acid could be prepared from a ton of sodium nitrate, 75% pure?

5. Sodium nitrate is much cheaper than potassium nitrate, but even though the cost were the same for each salt it would be more economical to use the sodium salt in making nitric acid. From a study of the equations involved show why this is true.

6. (a) How many litres of hydrogen are needed to combine with 10 litres of nitrogen? (b) How many litres of ammonia would be formed (all gases measured at the same temperature and pressure)?

7. What volume of air would convert 50 cc. nitric oxide into nitrogen dioxide? (Assume that air is $\frac{1}{5}$ oxygen and that all gases are at the same temperature and pressure.)

CHAPTER 25

Calcium and Magnesium

Two drams of chalk were converted into a perfect quick-lime, and lost two scruples and twelve grains in the fire. This quick-lime was slaked . . . with an ounce of water.

JOSEPH BLACK (1755)

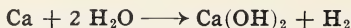
Calcium and magnesium are members of a family of elements known in the time of the alchemists as *earths* and subsequently called *alkaline earths* since they give an alkaline reaction with water. They occur in Group II of the Periodic Classification, have a positive valence of two, react with water liberating hydrogen, produce oxides that react with water to form bases, and displace hydrogen from acids. Calcium compounds are more common than magnesium compounds and have greater use in everyday life. Magnesium metal, however, is becoming increasingly important because it alloys readily with other metals, and can now be produced cheaply by the Pidgeon process from the extensive deposits of dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) occurring in Canada.

CALCIUM

Occurrence. Calcium is not found free in nature but occurs abundantly as a constituent of calcium carbonate in such familiar substances as limestone, marble, and chalk. Other important compounds, widely distributed across Canada, are gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$; calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$; fluorite, CaF_2 ; and apatite $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$.

Preparation. Metallic calcium is prepared by passing a direct current of electricity through fused calcium chloride in a graphite crucible serving as an anode. Calcium forms on one end of an iron cathode just touching the surface of the fused chloride, and as the calcium increases in thickness the cathode is gradually raised producing a long "cabbage stalk" of calcium which may be purified by distilling in a vacuum.

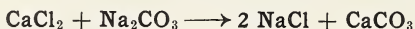
Properties and uses. Calcium is a silvery-white metal having a specific gravity of 1.55 and a melting point of 810°C . It burns in air with a brick-red flame to form a mixture of its oxide and nitride. Calcium readily decomposes cold water, liberating hydrogen in the process and leaving a deposit of the slightly soluble hydroxide.



Little use has been found for calcium metal. It is a component of a few important alloys of lead, and because of its great activity can be used as a reducing agent.

COMPOUNDS OF CALCIUM

Calcium carbonate (CaCO_3). Pure calcium carbonate (precipitated chalk) may be prepared in the laboratory by mixing aqueous solutions of calcium chloride and sodium carbonate.



It is insoluble in water, but reacts with acids to liberate carbon dioxide.

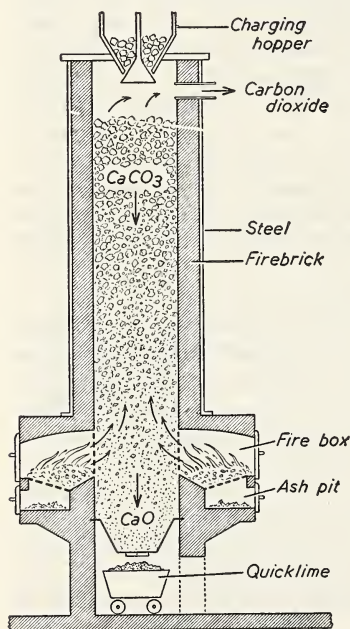
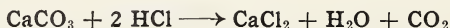
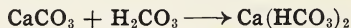
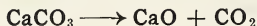


Fig. 25.1. Diagrammatic section of a vertical lime kiln.

It has a distinctive action with carbonic acid forming soluble calcium bicarbonate.



When calcium carbonate is heated to approximately 600°C ., decomposition occurs and calcium oxide and carbon dioxide are formed.

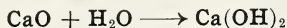


Calcium carbonate in its various forms is a very useful substance. Limestone is used as a building stone, as crushed stone for road building, and in the manufacture of quicklime, and cement. It is also used as a *flux* in the metallurgy of iron. Precipitated chalk is used as an abrasive in dentifrices.

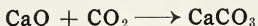
Calcium oxide (CaO). Calcium oxide (lime or quicklime) is prepared by heating limestone in kilns (Fig. 25.1). Pure lime is white, porous, and resistant to

heat. When heated to a temperature of 1800°C ., it gives off a brilliant light known as limelight. When a small amount of water is added

to a lump of quicklime, the lump cracks open, swells up, evolves steam, and produces a great deal of heat. This **slaking** causes the lump to crumble into a fine white powder known as slaked lime or calcium hydroxide.



If quicklime is exposed to air, it becomes "air slaked", combining with carbon dioxide to form the carbonate.



Quicklime has more than fifty common industrial uses, but its most important one concerns the manufacture of slaked lime.

Calcium hydroxide (Ca(OH)_2).

Calcium hydroxide (slaked lime) is a white powder sparingly soluble in cold water, and, contrary to the usual rules of solubility, less soluble in warm water. Its solution, a base, is known as *limewater*. A suspension of calcium hydroxide in water is called *milk of lime* and is sometimes used as "whitewash". Calcium hydroxide is used extensively in the making of mortar, plaster, and bleaching powder, with more limited uses in removing hair from hides, softening water of temporary hardness, and in the manufacture of other chemicals.



Gypsum Lime and Alabastine

Fig. 25.2. Mixing slaked lime, sand, and water in a mortar-box.

Mortar. Mortar is a mixture of slaked lime, sand, and water. When it is placed between bricks, its porous nature permits permeation of carbon dioxide from the air, with the resulting formation of hard, insoluble calcium carbonate which binds the porous bricks together



The original water, together with the water produced by the reaction, evaporates into the air.

Plaster. Plaster is essentially the same as mortar. Hair, or wood fibre, is added to make the mixture cling together better, and hardening may be promoted by burning charcoal in special burners, a procedure often followed in freshly plastered rooms.

Bleaching powder. When chlorine is passed into a box-like structure

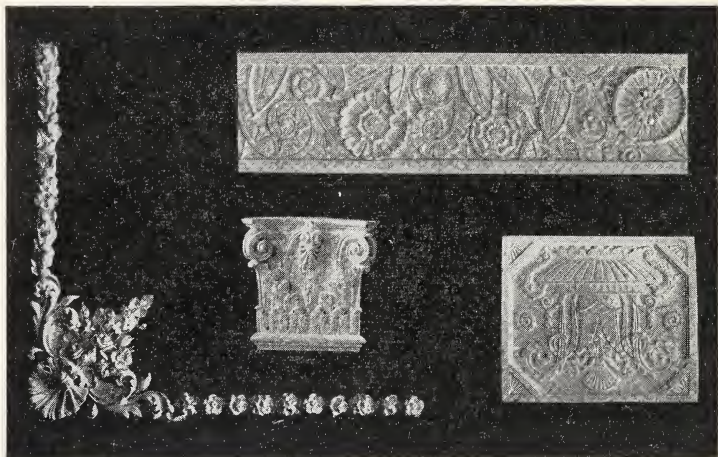
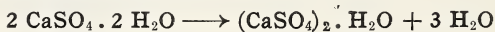


Fig. 25.3. Plaster of Paris frescoes. *Gypsum Lime and Alabastine*

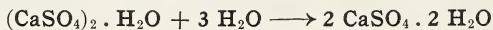
containing slaked lime spread on perforated shelves, two different compounds may be produced. One has the formula CaOCl_2 , and is commonly known as bleaching powder. The other compound is the calcium salt of hypochlorous acid known as calcium hypochlorite, $\text{Ca}(\text{ClO})_2$. This mixture is used in textile bleaching and in disinfectants.

Calcium sulphate (CaSO_4). Calcium sulphate occurs in limited quantities as the mineral anhydrite, but the most important occurrence is the soft mineral **gypsum**, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. It may be white or tinted with various colours. Its principal use is in the manufacture of plaster of Paris. When gypsum is carefully heated to approximately 150°C ., three-quarters of the water of hydration is driven off, and a white powder, known as plaster of Paris, is left.



Gypsum is also used in sizing paper, in making fire-proof plaster board, as a filler in paints, and as the chief component of blackboard chalk.

Plaster of Paris [$(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$]. Plaster of Paris is a white powder that forms gypsum crystals when water is added.

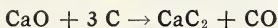


When plaster of Paris “sets”, it forms a smooth, white, hard, almost insoluble surface, useful as a finishing coat on plaster walls. Since it

expands slightly on setting, it is used in making statues and models of various kinds, and plaster casts for broken bones. The rate at which it sets may be controlled by means of accelerators such as common salt, and by retarders such as glue.

Calcium chloride (CaCl_2). Calcium chloride is obtained as a by-product in the Solvay process. It is a white, soluble solid crystallizing from water as the hexahydrate $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$. Being deliquescent, it is used on dusty roads because it attracts water from the air and forms a dust-laying solution. Since its saturated solution does not freeze until -55°C ., it is used to melt ice on roads and walks. It is also used in refrigerating solutions. Calcium chloride, added to concrete, increases the rate at which it sets.

Calcium carbide (CaC_2). Calcium carbide is a greyish-black solid, produced by the action of quicklime on coke in an electric furnace.



In addition to its use in making acetylene, calcium carbide is one of the raw materials required in the manufacture of calcium cyanamide.

Test. Calcium compounds, when volatilized, impart a brick-red colour to a non-luminous flame. A clean platinum wire dipped in any calcium compound moistened with hydrochloric acid will give this same colour when held in a non-luminous flame.

MAGNESIUM

The chief uses of magnesium are in the manufacture of light alloys for the construction of airplane parts, and other equipment where strength and lightness are desired. It may be cast and used in household appliances and cooking utensils. The activity of finely divided magnesium finds practical use in flash-light powders, military flares, incendiary bombs, and pyrotechnics. When magnesium is connected to underground iron pipe lines or inserted in hot water tanks, it corrodes before the less active iron is affected; thus, the life-span of the iron is greatly increased.

There are two common methods of abstracting magnesium from its compounds. The first is the electrolysis of fused magnesium chloride, of which substance there is an inexhaustible supply in sea-water; the second is a method recently developed in Canada by Dr. L. M. Pidgeon whereby the abundant supplies of dolomite are used.

Magnesium is a silvery-white, malleable metal. It oxidizes and tarnishes in moist air because of the formation of a basic carbonate, but in dry air it is stable. In the finely divided form, it can be ignited in air, and it burns with an intensely white flame, producing a mixture

of the oxide and the nitride. In larger masses, magnesium will not burn unless heated above its melting point of 650°C .

The uses of some of the most important compounds of magnesium are listed below.

COMPOUNDS OF MAGNESIUM

NAME OF COMPOUND	FORMULA	PROPERTY	IMPORTANCE
Magnesium chloride	MgCl_2	White crystalline	Source of magnesium
Magnesium sulphate Epsom salt	MgSO_4 $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$	White salt	Cathartic, as a mordant, fireproofing textiles
Magnesium carbonate	MgCO_3	Decomposes when heated	Manufacture of magnesium oxide
Magnesium oxide	MgO	White powder	Refractory brick, heat insulation, antacid in medicine
Magnesium hydroxide (milk of magnesia)	$\text{Mg}(\text{OH})_2$	White powder	Laxative, antacid in medicine, dentifrices

THE HARDNESS OF WATER

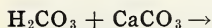
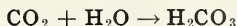
Water is said to be *hard* when it reacts with soap to form a white insoluble curd before producing a lather. Such water feels harsh to the skin. Water is *soft* when it readily lathers with soap. Soap consists of the sodium or potassium salts of certain organic acids derived from fats. Soaps are soluble in water and show a remarkable tendency to form "suds", helpful in removing grease from skin and clothing by emulsification.

Cause of hardness. Hard water contains much dissolved matter, especially salts of *calcium* and *magnesium*, present as the *bicarbonates*, *sulphates*, and *chlorides*. In some localities, soluble iron salts add to the hardness of the water. For purposes of convenience, hardness is classified as *temporary* and *permanent*.

Temporary hardness. Water is said to be temporarily hard when the hardness can be removed by boiling. Temporary hardness may be referred to as *carbonate hardness* because it is attributable to the bicarbonates of calcium and magnesium. It is removed by boiling because these soluble bicarbonates are decomposed to form the normal carbonates which, being insoluble, precipitate out of solution and therefore do not react with soap.



Calcium bicarbonate is a unique compound in that it can exist only in solution. Its presence in hard water is explained by the dissolving action of carbonic acid on limestone. Carbonic acid is formed when rain dissolves carbon dioxide from the air. Additional carbon dioxide is added to ground water by the respiration of aquatic life, and from the decomposition of organic materials. Coming in contact with limestone in soils or on lake bottoms, etc., the carbonic acid reacts with calcium carbonate to form the soluble bicarbonate which dissolves in the water.



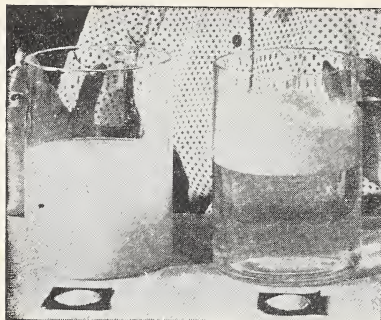
Underground water at depth, and so under considerable pressure, usually is rich in dissolved carbon dioxide (carbonic acid), and therefore capable of dissolving a great deal of calcium carbonate. Hence, in some limestone regions huge underground caverns have formed as a result of thousands of years of this dissolving action. Water seeping through the roofs of such caverns releases some carbon dioxide because of the sudden decrease in pressure, and limestone comes out of solution causing stalactites to hang from the roof. Stalagmites may form on the floor because of the evaporation of the fallen water.

Permanent hardness. Because *non-carbonate hardness* cannot be removed by boiling, it is called permanent hardness. It is caused by the presence of the sulphates and chlorides of calcium and magnesium in solution, and boiling does not remove the hardness since these are not affected by heating. To remove permanent hardness it is necessary to add some chemical capable of precipitating the calcium and magnesium in the form of insoluble compounds. One of the cheapest and



Luray Caverns

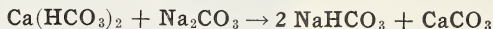
Fig. 25.4. An underground cavern at Luray, Virginia. Stalactites and stalagmites are in profusion. Near the centre of the photograph a stalactite and a stalagmite have met and combined to form a column of stone.



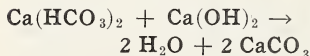
Permutit Company

Fig. 25.5. Hard and soft water. Equal amounts of soap have been added to the water in each container. The water on the right had previously been softened with permutit. Note the absence of curd and the abundance of lather in the softened water.

is not practical to soften large amounts by boiling.



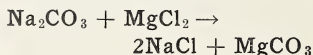
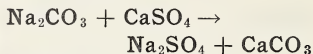
Slaked lime, useless for removing permanent hardness, is useful for softening temporarily hard water.



In the permutit process, hard water is passed through permutit (sodium aluminum silicate) that reacts with the calcium and magnesium to form insoluble compounds. When the permutit has been exhausted, it may be regenerated by treatment with common salt.

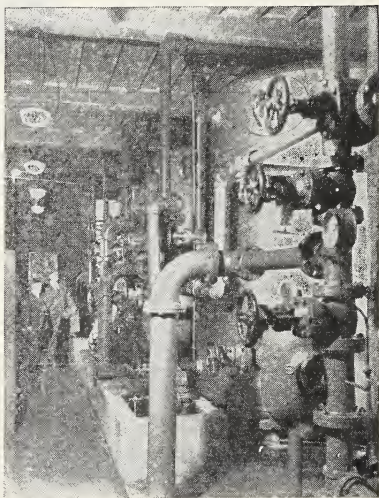
Hardness in water creates a serious problem in industry. The loss in heat transfer by the deposition, inside boilers, of such insoluble substances

most efficient chemicals used to soften water is washing soda. It exchanges sodium for the calcium or magnesium of the hard water to form insoluble carbonates.



Other chemicals sometimes used are borax, trisodium phosphate, and permutit.

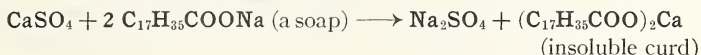
The above named chemicals may also be used to soften temporarily hard water as it



C. I. L.

Fig. 25.6 This municipal water softening plant at Etobicoke, Ontario, uses 300 tons of salt a month in restoring the permutit used in softening water.

as scale results in great losses in energy. In addition, the replacement of boiler tubes entails considerable expense. When soap is used for washing purposes in the home, much of it is wasted in precipitating the insoluble curd before the soap can produce the required lather.



Soapless detergents do not form insoluble curd. One of the most common is sodium laural sulphate sold under many different trade names. Besides leaving no insoluble curd or scum, these detergents produce an abundant lather in hard as well as in soft water.

EXERCISE

A

1. Why are calcium and magnesium known as alkaline earths?
2. State four properties common to both calcium and magnesium.
3. Name seven common substances containing calcium.
4. In the metallurgy of calcium, why is the crucible anode made of graphite? Why would it be inadvisable to make the anode of iron? Why is distillation of the cathode product necessary?
5. State six properties of calcium.
6. What property of calcium carbonate makes it possible to prepare it from aqueous solutions of calcium chloride and sodium carbonate?
7. (a) Write equations, one for each, to show the action of (i) hydrochloric acid and (ii) carbonic acid on limestone. (b) In what way are the reactions in (a) different? In what way are they similar?
8. State six uses of the various forms of calcium carbonate.
9. (a) Describe the commercial preparation of quicklime. Give the equation. (b) Trace the reactions that take place from the time quicklime is produced until a brick building in which it has been used has been completed (including plastering) for several years. Write equations to illustrate the reactions.
10. (a) Describe (i) the visible and (ii) the chemical changes that occur when quicklime is slaked. (b) What precaution must be taken when quicklime is slaked in the laboratory? (c) Why is quicklime that has been air-slaked not fit for use?
11. Limewater is sometimes given to babies as a medicine. What useful purpose does it serve?
12. (a) How is mortar similar to and different from plaster? (b) What is whitewash, and what chemical change occurs after it is applied to a surface?
13. (a) Describe how bleaching powder is used in textile bleaching. Explain the bleaching action. (b) Write equations to confirm the statements made in (a). (c) Why is bleaching powder more suitable than chlorine for bleaching textiles?
14. (a) Why is the fact that gypsum occurs naturally (as a hydrate) important? (b) Name three important properties of gypsum that make it useful and state the property upon which each use depends.
15. (a) Name five properties of plaster of Paris and give five different uses dependent on these properties. (b) Write one equation that would explain all these uses.

16. (a) By means of suitable equations, show how calcium chloride may be obtained from the Solvay process. (b) Name five uses of calcium chloride and give one property upon which each use depends.

17. (a) What is the advantage of using an electric furnace to make calcium carbide? (b) Why is commercial calcium carbide often dark in colour?

18. (a) Write the equations for the action of calcium carbide on (i) water and (ii) nitrogen. (b) In your opinion, which of these reactions is of greater importance to mankind? Explain your answer.

19. Why does calcium have to be volatilized before it can be identified by a flame test? What colour does calcium give to a non-luminous flame?

20. Give the name and the formula of a calcium compound that finds everyday use in (a) making plaster; (b) making quicklime; (c) laying dust; (d) bleaching cotton; (e) making fertilizer; (f) making a fuel; (g) making statues.

21. Name a simple test that could be given to distinguish between the following pairs of solids: (a) calcium carbonate and calcium sulphate; (b) gypsum and plaster of Paris; (c) quicklime and slaked lime; (d) slaked lime and air-slaked lime; (e) calcium carbonate and magnesium carbonate; (f) calcium carbide and calcium cyanamide.

22. (a) What properties of quicklime make it useful in producing *limelight*? (b) Why is the phrase "in the limelight" losing its practical significance?

23. A lighted charcoal burner will make a freshly-plastered house more quickly habitable. Why?

24. Explain why a road sprinkled with calcium chloride will appear damper in the early morning than in late afternoon.

25. Suggest how a chemist would explain the formation of (a) an underground cave in a limestone region; (b) a stalactite; (c) a stalagmite; (d) the presence of excessive amounts of carbon dioxide near the floor of the cave.

26. (a) Give four uses of magnesium. (b) What properties of magnesium alloys make them particularly suitable for the construction of airplane parts?

27. Large castings of magnesium do not present a fire hazard whereas magnesium ribbon and finely-divided magnesium are potentially dangerous in this respect. Explain.

28. (a) Name and give the formulae of five magnesium compounds. Write the formulae for the corresponding calcium compounds. (b) Give a use for each of the magnesium compounds named in (a) and state the property upon which each use depends.

29. (a) What is the cause of (i) temporary hardness and (ii) permanent hardness of water? (b) Which type of hardness may be removed by boiling? Explain why boiling is effective. (c) Explain why it is difficult to form a lather with soap and hard water.

30. (a) How may permanently hard and temporarily hard water be distinguished from each other? (b) Why is rain water better than spring water for laundry purposes?

31. What chemical reactions take place in (a) the softening of permanently hard water; (b) the softening of temporarily hard water; (c) the formation of a curd when hard water is added to a soap solution?

32. (a) Explain why permanently hard water is softened by the addition of washing soda. Give the chemical equation involved. (b) What type of hardness of water may be removed by boiling the water? Give the chemical equation involved. (c) Explain why soap is wasted when hard water is used for laundry purposes.

33. Hardness in water presents three serious problems. Name these problems and explain the methods used to control them.

34. What are the advantages of the soapless detergents as compared to soap?

B

1. What weight of quicklime could be made from one ton of 95% pure limestone?

2. What weight of sulphuric acid will be required to neutralize 50 gm. calcium hydroxide?

3. What weight of plaster of Paris could be obtained from 100 pounds of gypsum?

4. Find the percentage of water in (a) gypsum, (b) plaster of Paris.

5. What weight of water would be required to slake 1 kilogram of quicklime?

6. (a) What weight of chlorine would be required to make 500 grams of bleaching powder? (b) What volume would this chlorine occupy at 23° C. and 748 mm. pressure?

CHAPTER 26

Chemistry in Industry

I do not like the phrase, "Never cross a bridge till you come to it."
The world is owned by men who cross bridges on their imaginations
miles and miles in advance of the procession.

BRUCE BARTON

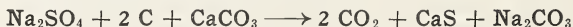
The discoveries of yesterday, though miracles in their own right, are claimed as today's birthright, and have become a component of the normal way of modern living. No longer do radios, telephones, motor cars, and airplanes cause any flurry of excitement, and young people today accept nylon, cellophane, television, and lucite as essential commodities, just as their parents accepted the steam engine and the power loom.

Few people, using modern inventions and modern materials, realize that these were made possible by a better understanding of the chemical nature of things, by improvements chemistry effected in familiar substances, and by the creation, through chemistry, of a whole range of new substances when the old ones failed to meet the current needs.

The entire chemical industry has been founded upon the desire to create something new from something old by means of deliberate scientific processes. It dates from the year in which Lavoisier lost his head on the guillotine during the French Revolution. The French had been receiving essential supplies of alkali for their glass factories from Spain, but when the British cut off this supply from reaching France, the French Academy offered a prize of 100,000 francs for a process ensuring a plentiful supply of soda ash. In 1784, Nicolas Leblanc started work on the problem, and after three years of experimentation and deliberate planning, he evolved a process whereby sodium carbonate could be produced from common salt and sulphuric acid. A simple equation will show that sodium sulphate is a product of this reaction:



However, Leblanc showed that when sodium sulphate was heated with coke and limestone, sodium carbonate was produced and could be isolated by extraction with water:



At a reasonable price, caustic soda could be obtained from the sodium carbonate by treating it with slaked lime:



Leblanc was unique in that he did not discover something just by accident from the then-known industrial chemistry. Rather, by deliberate logical reasoning, he used industrial chemistry, as it was known to him, to create something new.

Leblanc's history-making discovery illustrates two characteristic features of chemical industry. In the first place, while Leblanc was working to improve the economic status of France, and at the same time to bolster his own economic position, he had no idea of the number of new industries to be born because of his single discovery. To cite only one example: soap was a luxury enjoyed only by a few because its manufacture required a strong, expensive alkali, but with the appearance of a cheap base, an expanding soap industry brought a new concept of personal hygiene to the masses, along with a new and cheaper method of whitening cloth without sunshine. More alkali demanded more sulphuric acid; so new and better methods were required not only for the production of the acid but for all of the related chemicals, and hence a great expansion occurred in a large number of fields. In the second place, remarkable as was Leblanc's discovery, his process was soon discarded for the new and better Solvay process for making sodium carbonate. Today, soap is facing the competition of detergents or "soapless soaps", and if these new products prove their superiority, chemical industry will see to it that soap meets the same fate as did the Leblanc soda process. New substances will always replace old, unsatisfactory ones.

While Leblanc gave chemical industry its start in the 18th century, the 19th century marked a period of phenomenal growth in basic discoveries. Analine, the first synthetic dye from coal tar, was discovered in 1856 by William Henry Perkin. In 1863, Ernest Solvay introduced an alkali process using salt, carbon dioxide, and ammonia as basic materials. The iron and steel industries expanded quickly, and it was discovered that foul-smelling petroleum or "burning oil" could be subjected to fractional distillation to produce a host of valuable and, heretofore, unknown products. Volta, in 1810, established the principle of electrolysis, and by the end of the century electrical power had been developed at Niagara Falls, enabling Charles Martin Hall to perfect an electrolytic process for producing cheap aluminum. Frasch succeeded in bringing sulphur from underground by the surprisingly simple method of melting it with hot water and forcing it to the surface by means of compressed air.

The progress of the 20th century, although owing much to the

CHEMISTRY IN INDUSTRY

Primary Materials	Secondary Products and	Subsequent Reactions	Uses
Water	Water gas		Fuel Hydrogen source Alcohol source
Coal	Carbon monoxide		Gaseous fuels Reducing agent Nickel purification Methyl alcohol
	Hydrogen		Antifreeze Solvent Making formaldehyde Denaturant
	Methyl alcohol		
Limestone	Calcium oxide		As a fertilizer Making organic compounds
	Nitrogen		
	Calcium cyanamide		
	Calcium carbide		Making acetylene Calcium cyanamide
Water	Acetylene		Illuminant Oxy-acetylene torch Synthetic rubber Synthetic fabrics
Air	Oxygen		
	Nitrogen		
	Cellulose		Solvent Textile industry Rayon Cellulose acetate
	Cellulose acetate		
Salt	Hydrogen		Rayon Textiles Plastics Film for motion pictures
	Ammonia		Making fertilizers As a refrigerant Household ammonia Smelling salts
Water	Sodium bicarbonate		Baking soda & baking powders To make washing soda As an antacid In fire extinguishers
	Sodium carbonate		A water softener Making glass Soap To make pure baking soda
Limestone	Carbon dioxide		Fire extinguishers In soft drinks As "dry ice" Making "white lead"
Air	Oxygen		Bleaching agent As a refrigerant In fumigation As a preservative
	Sulphur dioxide		
Sulphur	Sulphur trioxide		In the manufacture of sulphuric acid
Water	Sulphuric acid		Making fertilizers Refining petroleum Making other chemicals To make explosives
Salt	Hydrochloric acid		Cleaning metal surfaces Making glue Production of corn syrup Making textiles & dyes

The chart shows the raw materials and the main stages that lead to the production of many finished products. It is also designed to be used as a guide for the more intensive study of any specific product. Source material for this study is to be found in a great variety of textbooks and in the wealth of material made available free of charge by the many Canadian industrial companies that produce these products. For example, a further study will reveal the following facts about rayon:

Coal, sulphur, and salt are the raw materials required. Coal, subjected to destructive distillation, produces coke. When coke and sulphur are heated in an electric furnace, they unite chemically to produce carbon disulphide, which distills off as rapidly as it is formed.

When a direct current of electricity is passed through a solution of common salt, a

CHEMISTRY IN INDUSTRY

Primary Materials	Secondary Products and Subsequent Reactions	Uses
Salt	Chlorine	Water purification Bleaching
Sulphur	Carbon tetrachloride	Fire extinguisher Cleaning fluid
Coal	Coke	Carbon tetrachloride Solvent Insecticide
	Carbon disulphide	Rayon Cellophane
	Cellulose	Viscose
		Rayon Cellophane Textile fibres Packaging materials
Salt	Caustic soda	Manufacture of chemicals Rayon and cellulose
	Chlorine	Petroleum refining Lye, paper, soap
	Sodium hypochlorite	Bleaching Antiseptic solution
Limestone	Quicklime	Bleaching powder
	Slaked lime	Bleaching fabrics In swimming pools
		Plaster and mortar Slaked lime
		Slags in metallurgy Making other chemicals
Water	Cellulose	Nitrocellulose
		Explosives Motion picture film
Air	Oxygen	Nitric acid
	Nitrogen	Ammonia
		Making fertilizers Explosives
Salt	Hydrogen	As a refrigerant Ammonium hydroxide Explosives
		Making fertilizers
Coal	Coal tar	Hydrogenation of oils Welding and cutting
	Coke	As a fuel
	Ammonia	Dyes Perfumes Drugs Explosives
		Fuel Metallurgy of iron
		Calcium carbide Water gas
		Making baking soda Nitric acid
		Ammonium sulphate

solution of caustic soda is one of the resulting products. In an 18 per cent caustic soda solution sheets of purified bleached sulphite wood pulp (cellulose) are steeped for about two hours. The resulting alkali-cellulose is shredded to a fine "crumb" and stored in steel cans to age. Then, it is treated with carbon disulphide to form a product known as cellulose xanthate, which dissolves in a solution of 4 per cent sodium hydroxide to form a liquid that looks like thick honey. This liquid is known as viscose solution.

A most interesting chemical transformation occurs when this viscous liquid is forced through tiny holes in a spinneret into a dilute solution of sulphuric acid, where it hardens into strands of extremely fine fibres of cellulose. Once these strands are washed free of the adhering solution, bleached, and washed again, the rayon is ready to be woven or knitted. The resulting fabric may then be dyed, rendered crease-resistant, water-repellant, or fire-proof, depending upon the use to which it will eventually be put.

discoveries of the past, is further proof of the amazing ingenuity of man. The products of modern chemical industry are so varied they stimulate the most lethargic imagination. It is difficult to believe that practically all of the products we use come from the simple primary materials, coal, limestone, salt, wood, sulphur, air, and water. A few of these transformations have been represented on pages 272 and 273, but the mention of all is beyond the scope of this book. Every product has a story that reads like a fairy tale, and all can read with interest the wealth of accurate literature provided by the great industries of today.

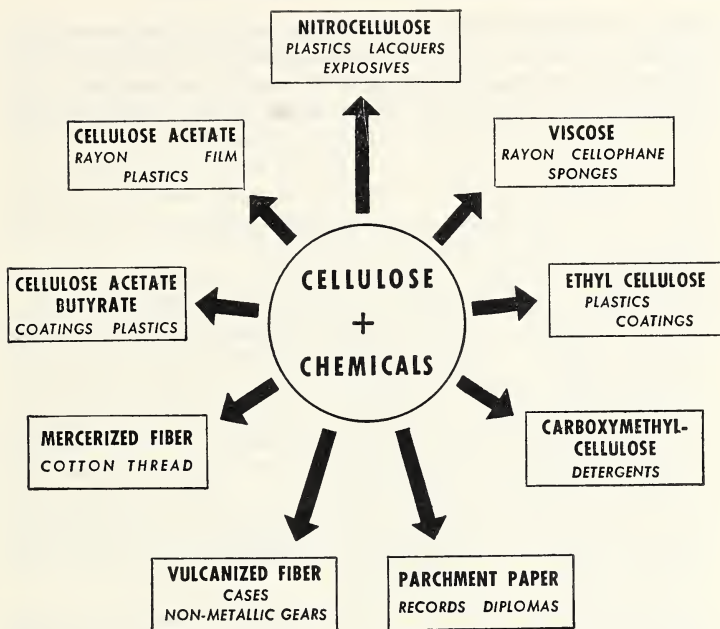
Our dependence upon chemistry is evident when we carefully examine our surroundings. Imagine, if you can, life without glass, alloys, soap, plastics, rayon, paint, paper, ink, insecticides, gasoline, leather, rubber, processed foods, silicones, radio, television, and aspirin! Yet these are only a few of the countless thousands of substances and commodities that form an integral part of modern living and that owe their existence to the magic of the chemist.

ALLOYS

Reference was made in Chapter 25 to the use of calcium and magnesium in alloys. Metals and some non-metals possess the property of dissolving in one another to form solid solutions. Sometimes the components do not form a true solution, but the mixture (alloy) possesses properties new and different from either of the original components, and a never-ending variety of properties may result by varying the proportions of the components. Following is a list of a few common alloys.

COMMON ALLOYS

ALLOY	MAIN COMPONENTS	USES
Brass . . .	copper, zinc	jewelry, hardware, musical instruments, cartridge cases
Sterling silver	silver, copper	silverware, jewelry
Nickel coin .	copper, nickel	coinage
Silver coin .	silver, copper	coinage
Monel metal	nickel, copper	chemical equipment, sinks, tables, cooking utensils
Steel . . .	iron, silicon	transformer cores
	iron, cerium	lighter flints
	iron, manganese	teeth for steam shovels
	iron, tungsten	high speed cutting tools
	iron, chromium	stainless steel cutlery and food-processing utensils
Solder . . .	tin, lead	joining metal surfaces
Magnalium .	magnesium, aluminum	automobiles, speed boats, general construction
Duralumin .	aluminum, copper, manganese, magnesium	airplane and general construction



E. I. du Pont de Nemours

Fig. 26.1. Cellulose products.

CELLULOSE PRODUCTS

Ever since the human race was in its infancy, men have depended upon wood and cotton. They have burned wood for fuel, and converted it into furniture, houses, boats, paper, and many other products. By distilling it in the absence of air, they have obtained wood alcohol, charcoal, acetic acid, tar, and other valuable products. They have made cotton into such products as cloth, paper, and surgical dressings.

Cellulose began its career as a chemical raw material in 1845 when "guncotton", or nitrocellulose, was first produced. The achievements in this field of chemistry, like those in the field of plastics, have been so phenomenal that space does not permit a recording of them. The above chart, taken from "The Story of Cellulose" by E. I. du Pont de Nemours & Co., gives a glimpse of the possibilities of cellulose chemistry.

PLASTICS

The Committee on Plastics Education of the Society of the Plastics Industry, Inc., has defined a plastic as "any one of a large and varied

group of materials which consist of, or contain as an essential ingredient, an organic substance of large molecular weight, and which while solid in the finished state, at some stage in its manufacture has been or can be formed into various shapes by flow, usually through application singly or together of heat and pressure."

The committee reaffirms the statement made previously that the origin of plastics is another example of the age-old search for new and better materials to replace natural ones, or to perform functions more satisfactorily than materials already in use.

In 1868, a prize was offered for a substitute for ivory from which billiard balls were made. John Wesley Hyatt, a printer from Albany, New York, devised a method of mixing cellulose nitrate with camphor, and the resultant product, *celluloid*, became the first commercially accepted plastic. In 1895, shellac was utilized to make phonograph records, and in 1909 Dr. Baekeland, a Belgian chemist living in the United States, produced a plastic from phenol (carbolic acid) and formaldehyde, capable of being molded under heat and pressure into a variety of products. In 1919, casein plastics, made from the protein of skim milk and formaldehyde, became a commercial product. Since 1925, a tremendous increase in the annual production of plastics has occurred.

Plastics are divided into two general types, viz. *thermosetting* and *thermoplastic* resins. "Thermo" means heat, hence the thermosetting group comprises those plastics which set or harden into permanent shape when heat and pressure are applied to them, whereas the thermoplastic group includes those that are softened by heat and then hardened into shape by cooling. Both of these types are light in weight,

COMMON THERMOSETTING PLASTICS

CHEMICAL NAME	TRADE NAME	PROPERTIES	USES
Melamine-formaldehyde	melmac plaskon	moisture resistant surface hardness light-fast colour	buttons table ware crease-proofing of textiles
Urea-formaldehyde	bakelite plaskon	light-fast colour acid-alkali resistant	radio cabinets lighting equipment electric razors
Phenol-formaldehyde	bakelite durez	easily molded and cast temperature resistant chemical resistant excellent insulating properties	telephones electrical switches radio cabinets costume jewelry buttons

and have great strength in proportion to their weight. They are warm to the touch, have good insulating properties, and can be produced in a wide range of colours which completely permeate the finished articles. The accompanying tables indicate some of the properties and uses of the common plastics.

COMMON THERMOPLASTIC PLASTICS

CHEMICAL NAME	TRADE NAME	PROPERTIES	USES
Methyl methacrylate	lucite plexiglas	excellent optical properties soft, light weight shatter and weather resistant	lenses airplane windows surgical apparatus costume jewelry powder boxes
Caseins	ameroid galorn	good lustre and colour range deteriorate in high humidity	buttons toys novelty jewelry
Cellulose acetate .	bakelite plastacele	excellent water resistance easily molded wide colour range	combs tooth brushes toys transparent containers
Cellulose nitrate . . (pyroxylin)	celluloid pyralin nixonoid	cannot be molded tough, flexible water resistant inflammable	shoe heel covers fountain pen barrels piano keys photographic film ping pong balls Fabrikoid "Px" cloth for book binding
Cellulose propionate	forticel	great toughness low specific gravity low water absorption resistance to warping	steering wheels flashlights optical frames tooth brushes
Ethyl cellulose . . .	ethocel	tough and flexible at low temperatures acid-alkali resistant	radio cabinets steering wheels flashlights vacuum cleaner parts packaging material
Polyamides	nylon	light, tough, flexible resistant to chemicals may be molded or made into filaments	hosiery brush bristles tennis racquet strings tumblers, slide fasteners, fishing lines

COMMON THERMOPLASTIC PLASTICS—*Continued*

CHEMICAL NAME	TRADE NAME	PROPERTIES	USES
Polyethylenes . . .	polythene	chemically inert flexible, tough	wire and cable insulation shower curtains packaging
Polystyrenes . . .	lustron styron	low water absorption chemically resistant	instrument panels battery cases cosmetic containers household items
Tetrafluoroethylene .	teflon	withstands high temperatures chemically inert excellent dielectric	gaskets high frequency insulation containers for hot corrosive liquids
Vinyl resins . . .	vinylite	soft, tough relatively inert	safety glass inter- layer shower curtains shoe soles rainwear cosmetic containers
Vinylidene chloride .	saran	soluble in many solvents—properties similar to vinyl resins	coated fabrics transportation seating insect screening film
Polyacrylonitrile . .	orlon	light, tough, flexible, equivalent wet and dry properties, sun- light, weather, and temperature resistant	textiles awning fabrics suits overcoatings

NYLON

It took \$27,000,000.00 and 10 years' work to place the first strands of nylon on the market.

The story of nylon goes back to 1928 when a group of research chemists of the Du Pont Company in the United States, led by Dr. W. H. Carothers, undertook a program of what they called "fundamental research". Their work was not aimed at the creation of new chemical products or the improvement of existing ones. Instead, they hoped to discover new and fundamental facts about chemical materials and processes that would add to the basic knowledge necessary to all chemical advancement.

Dr. Carothers and his assistants were particularly curious about how and why certain molecules, of which all things are made, often

unite to form "giant" molecules. Many of these giant molecules exist in nature and are the principal building blocks of such well-known substances as cotton, rubber, silk and resins.

One of the facts the scientists uncovered after months of work was that they could make in the laboratory a new type of giant molecule that differed from those known to exist in nature, in that it was made up of molecules joined together in an orderly end-to-end manner, much like a chain of paper clips.

In 1930, while investigating this new discovery, one of the chemists made a startling observation. He removed a sample containing these giant molecules from the chemical still in which it had been made and noted that the molten sample could be stretched like warm taffy candy. Even after it had cooled, it still could be stretched to three or four times its original length.

More important, the chemist saw that when the sample was so drawn it became much stronger and more elastic, a development never before seen in such substances. The chemist wondered whether it might not make an excellent textile yarn.

After studying these new compounds for seven years, the chemists were finally able to produce greatly improved substances known as "linear polymers". These appeared on the market in 1938 as bristles for tooth brushes and proved superior in many ways to natural bristles. Then, with the co-operation of the hosiery industry, a yarn suitable for women's stockings was developed; on May 15, 1940, the first nylon stockings went on sale.

Nylon proved stronger, tougher, and more durable than any natural fibre. It was found to resist abrasion, damage by moths or mildew, had great dimensional stability and high wet strength, and was easy to launder, quick to dry, and light to wear or carry.

As its unique qualities became better known, nylon, as a yarn, staple fibre and plastic, was quickly adopted in other fields. Today, it is used in hundreds of products found in home and factory, ranging from baby garments and stockings to ropes for rope-driven machinery.

Construction of a Canadian nylon plant began in 1940, and the first nylon made in Canada came off the machines at the Kingston, Ontario, plant of Canadian Industries Limited on June 26, 1942.

The manufacture of nylon is a complicated chemical process. Basically, the fibre is derived from coal, air, and water, beginning with the production of benzene from coal tar, nitrogen and oxygen from the air, and hydrogen from water.

Combined and subjected under exacting control to a succession of chemical reactions, the resulting product is nylon salt which is soluble

in water, the form in which it usually is transported or stored.

The second major step is to convert the nylon salt from a liquid to a solid. The solution is pumped from storage tanks to an evaporator and thence to a giant pressure cooker called an autoclave. Here, the molecules of the nylon salt are joined end-to-end to form the very large molecules called superpolymers. These help to give nylon its toughness and elasticity.

The molten mass then is extruded through a narrow slit on to a large polished drum where the white ribbon of nylon is solidified and cooled by water sprays that harden it as it moves along to the chipper, a rotary cutter that chops the nylon ribbon into hard, ivory-like flakes about the size of soap flakes.

The third major operation begins when the nylon flakes are dumped into a hopper, melted, and the molten nylon pumped through the tiny holes of a small metal plate called a spinneret.

As the molten nylon is extruded from each hole, it solidifies as a filament. These filaments are twisted together to form the yarn known as multifilament. The filaments are then wound on bobbins, completing the operation known as spinning.

The yarn is next stretched about four times its original length and twisted by running it through a draw-twisting machine. This operation gives the yarn the strength, elasticity, translucence, and lustre for which it is noted.

ORLON

Orlon, like nylon is a truly synthetic fibre, possessing properties enjoyed by neither natural nor earlier synthetic fibres. It has high strength, ability to be stabilized, excellent durability, and properties that are essentially the same whether wet or dry. It is resistant to sunlight, weather conditions, and high temperatures. Comparative tests have indicated that under light and weather exposure orlon retains 80% of its original strength after other organic fibres have disintegrated.

In the staple fibre form orlon produces fabrics which are sufficiently strong and warm, without being heavy. These fabrics have the most wool-like feel and appearance of any known synthetic fibres. Suitings and overcoatings made from orlon have good appearance and make excellent materials for rugged winter climates. When formed as a continuous filament it is the most silk-like synthetic fibre known. Because it is a thermoplastic plastic it has excellent press retention under wet as well as dry conditions; thus a dampened orlon suit will dry to its original appearance.

The chemist has created, within a single generation, a host of new materials, many possessing seemingly unbelievable properties. Public acceptance of rayon, nylon, orlon, and the great variety of other synthetics indicates that these substances can be commercially successful if they have specific characteristics better than those of previously known fibres, and if they can be manufactured economically. Chemists, with their ability to synthesize new materials, will make possible even more spectacular fibres, whose properties will be determined by the precise application for which each is required.

EXERCISE

A

1. (a) What fundamental principle served as the basis for the founding of chemical industry? (b) What incident was responsible for the beginning of the chemical industry? (c) How does *chemical industry* differ from *industrial chemistry*? (d) Name two characteristic features of chemical industry.

2. (a) Write equations to represent (i) the Leblanc method and (ii) the Solvay method for making sodium carbonate. (b) Why is the Solvay method considered to be superior to the Leblanc method? (c) Describe the modern method of obtaining sodium hydroxide. How is this method superior to the Leblanc method?

3. (a) Name seven basic discoveries made in the 19th century. (b) Name five basic discoveries made in the first fifty years of the 20th century.

4. (a) What is meant by the term *alloy*? (b) Name five common alloys, give their main components and state one important use for each alloy.

5. (a) Define the term *plastic*. (b) Name the two general types of plastics and explain the meaning of each term.

6. (a) Name three common thermosetting plastics, state one important use of each and give the property that makes this use important. (b) Name five common thermoplastic plastics, state one use of each and give the property that makes this use important.

7. Name ten different ways in which cellulose has been useful to man. Illustrate your answer with suitable examples.

8. Name five common substances that depend for their formation on (a) coal; (b) air; (c) water; (d) sulphur; (e) limestone; (f) salt; (g) cellulose.

9. How many of the thirty-five substances named in the above question have entered directly or indirectly into your life? Explain.

10. Describe briefly the industrial process involved in making each of the following chemicals: (a) sulphuric acid; (b) nitric acid; (c) hydrochloric acid; (d) ammonia; (e) acetylene; (f) slaked lime; (g) gasoline; (h) bleaching powder; (i) methyl alcohol; (j) rayon; (k) nitroglycerine; (l) nylon.

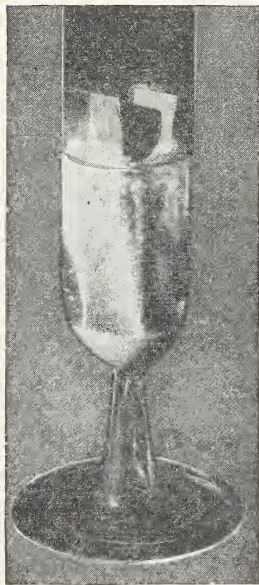
CHAPTER 27

The Metals

Metallurgy, the oldest of arts and the newest of sciences.

GENERAL MOTORS, (*Metallurgy and Wheels*)

Most substances can be classified in several ways and the elements which form the basis of the study of chemistry are no exception. In the classification dealt with here the elements are divided into two groups according to their ability either to give up or to accept electrons when they enter into combination to form compounds. Elements that give up one or more electrons act as metals, and elements that accept electrons act as non-metals (see page 135). Approximately 80% of the elements known to-day act as metals and give up electrons to return to a stable octet ring structure.

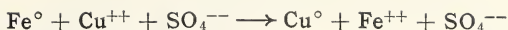


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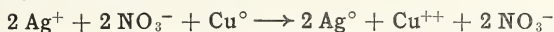
Fig. 27.1. A strip of copper in a solution of silver nitrate becomes coated with crystals of pure silver.

Properties of metals. To be classified as a metal an element must possess several physical and chemical properties in addition to the giving up of electrons during chemical combination. These properties are listed in the appendix, page 374. It should be remembered, however, that there is no sharp line of distinction between metals and non-metals for there are many exceptions to the general rule.

Order of activity of metals. Metals may be arranged in order of activity. If an iron nail is immersed for a short time in a solution of copper sulphate, a reddish deposit which may be proven to be metallic copper appears on the nail. If the procedure is reversed and a copper nail is used in an aqueous solution of an iron salt, nothing will happen. The chemical change in the first experiment shows that iron is more active than copper and that it has the power to displace copper from a solution of a copper salt in much the same way as chlorine displaces bromine (see Chapter 21). An ionic equation for the reaction may be represented as follows:



In a like manner a strip of copper dipped in a solution of a soluble silver salt becomes coated with white crystals of pure silver. (Fig. 27.1.) If the resulting solution is analysed, the presence of cupric ions will be indicated.



By similar experiments many of the metals may be arranged in order of their decreasing chemical activity, and by other methods all metals may be so arranged. If the position of the metal in the series is known, certain of its chemical properties can be predicted.

The following **Activity Table** includes some of the metals and serves to illustrate the above statement.

OCCURRENCE	ELEMENT	REACTIONS	SYMBOL	EASE OF REDUCTION
Never found free in nature.	Potassium Sodium Calcium	React with cold water to produce hydrogen.	K Na Ca	Very difficult. May be reduced by the electrolysis of fused hydroxide or chloride. See page 214.
	Magnesium	React with hot water to produce hydrogen.	Mg	
	Aluminum Zinc Chromium	React with dilute acids to produce hydrogen.	Al Zn Cr	Reduced by metal replacement or by electrolysis.
Rarely found free in nature.	Iron		Fe	Oxides reduced by carbon or hydrogen.
	Tin	Concentrated hot HCl reacts to produce hydrogen.	Sn	
	Lead		Pb	
	Hydrogen	Oxidizing acids such as concentrated sulphuric acid and nitric acid react to produce gases other than hydrogen.	H	
Frequently found free in nature.	Copper Mercury Silver		Cu Hg Ag	
Usually found free in nature.	Platinum Gold	React with aqua regia ($\text{HNO}_3 + \text{HCl}$) to produce the chloride.	Pt Au	Reduced by heat alone.

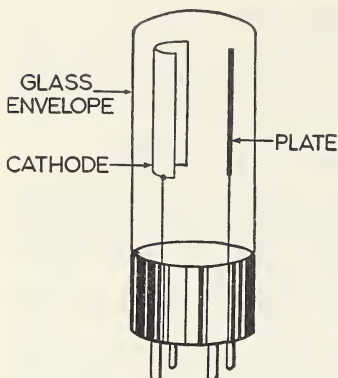


Fig. 27.2. The photoelectric cell. The plate in this electron tube is usually a single rod and is commonly called the anode target as the electrons emitted from the cathode are attracted to it.

its greater tendency to lose electrons. The members of the series below hydrogen will not react with dilute acids to liberate hydrogen. The elements above hydrogen will all react with most dilute acids to liberate hydrogen. The upper range of the series includes those metals that react with water to produce hydrogen.

The photoelectric cell. The tendency of the most active metals (cesium, rubidium and potassium) to give up electrons is so great that light falling upon the surface of the metal will cause electrons to be set free from the surface. This property coupled with the potential exerted by an electric current is utilized in the *photoelectric cell* (Fig. 27.2). The photoelectric cell when incorporated in a suitable circuit can be adapted to many domestic and industrial uses. For example, in a movie projector, the photoelectric cell is the unit which transforms light into sound. The sound track on a movie film is made up of light and dark areas. As these areas pass in front of a light focussed on

Although hydrogen is not considered to be a metal, it is included in the series because the hydrogen ion carries a positive charge. In addition, hydrogen can be displaced from dilute acids by metals above it in the series (see page 45). This reaction is possible because the metals above hydrogen have a greater tendency to give up electrons than has hydrogen, and hydrogen ions must have a greater tendency to gain electrons to form hydrogen atoms which combine to form molecules.

The higher the element is in the activity series, the more active it is. The element displays more metallic characteristics because of

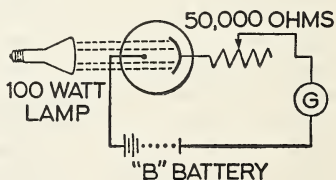
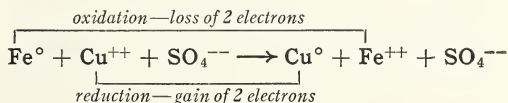


Fig. 27.3. The photoelectric circuit. Light from the lamp strikes the cathode of the photoelectric cell and causes electrons to be emitted. The electrons are attracted to the anode and pass to the positive side of the battery. The electrons lost by the cathode are replaced from the battery. This flow may be noted by the deflection of the galvanometer G. This current is too weak to be of any practical value unless it is amplified.

a photoelectric cell, electrical currents of varying strengths actuate the speaker producing sound.

Other uses of the photoelectric cell include the opening of doors, the inspection of merchandise, the matching of colours, the tripping of burglar alarms, the controlling of traffic, and the lighting of city streets and signs.

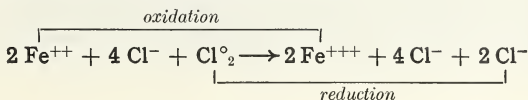
The electron theory and the activity series. When a free metal displaces a metal below it in the series from a solution of one of its soluble compounds, a transfer of electrons takes place. The free metal gives up its electrons and forms ions, and the metallic ions in solution take these electrons and form neutral atoms which appear as free metal.



In the above equation each electrically neutral atom of iron has given up electrons, and each copper ion in the solution has accepted two electrons from each atom of iron to become a neutral (metallic) copper atom. Iron has changed from the atomic form into the ionic form, and copper has changed from the ionic form into the atomic form. The sulphate ion remains unchanged.

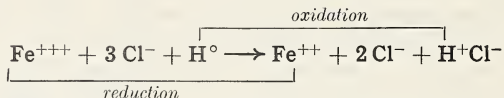
Oxidation and reduction. In the light of the modern theory of atomic structure, the term oxidation takes on a much broader meaning than given on page 25 where oxidation was defined as the union of a substance with oxygen. The iron in the above reaction is oxidized because it has lost electrons and increased in positive valence, whereas the copper has been reduced because the copper ions have gained electrons and decreased in positive valence.

This concept of oxidation and reduction in terms of change of valence illustrates that oxidation-reduction reactions may take place without the presence of oxygen. For example, consider the oxidation of ferrous chloride to ferric chloride. Ferrous chloride in solution may be prepared by treating iron with hydrochloric acid and filtering the mixture. If chlorine gas is bubbled through the pale green filtrate containing ferrous chloride, the solution takes on the amber colour characteristic of a solution of ferric chloride.



Each ferrous ion gives up an electron to a chlorine atom. This reaction causes the iron to be oxidized, and at the same time the chlorine is reduced. Reactions of this kind involving oxidation and reduction are sometimes referred to as **redox** reactions.

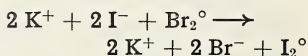
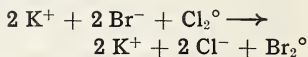
Another redox reaction takes place when a solution of ferric chloride is placed in an iron—hydrochloric acid hydrogen generator.



Here the ferric ion has gained an electron and has therefore been reduced, whereas each hydrogen atom has given up an electron to the iron and has therefore been oxidized.

Because oxidation and reduction involve only changes in valence, redox reactions take place with the non-metals as well as with metals. In addition to the example using chlorine given above, the replacement

of bromine and iodine by chlorine and the replacement of iodine by bromine are common examples of redox reactions.



The above ionic equations show that bromine and iodine have each been oxidized by the loss of one electron per ion. Chlorine is more active than either bromine or iodine and hence takes electrons from both the bromide ions and the iodide ions. The chlorine is therefore reduced forming chloride ions, and the bromine and the iodine are left in the atomic state.

Identification of metals.

One common way to identify certain metals is to apply a



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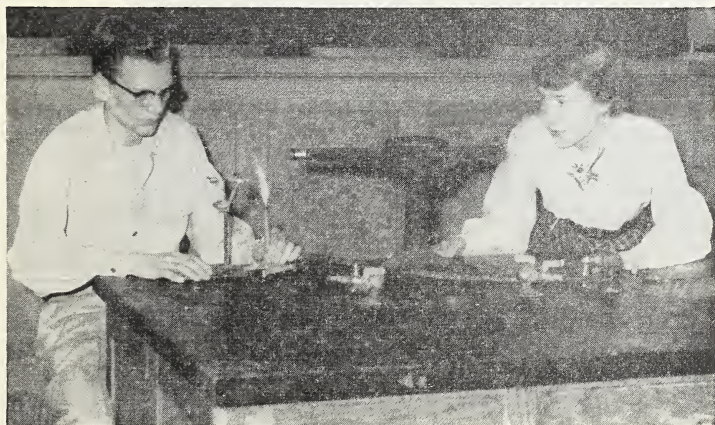
Fig. 27.4. A simple form of spectroscope. Light from the vaporized metal enters the tube (top left), is refracted through the prism and the bright-line spectrum is viewed through the telescope (top right). A light in front of the remaining tube brings a graduated scale into the field of vision.

flame test to the salt of the metal and note the colour imparted to the flame.

A piece of platinum wire, usually mounted in a glass rod, is cleaned by dipping the wire into a concentrated solution of hydrochloric acid, and then holding it in a non-luminous Bunsen flame. When the wire is perfectly clean, it glows red in the flame but imparts no colour to it. The wire is now dipped into a solution of the salt to be tested and placed once again in the flame. If a sodium salt is used, the flame takes on a rich, golden-yellow colour. If a potassium salt is used, the flame becomes violet. Other metals are characterized by their colours as follows:

Lithium.....	Crimson
Copper.....	Emerald-green
Strontium.....	Red (scarlet)
Calcium.....	Orange-red
Barium.....	Yellow-green

The spectroscope. The spectroscope (Fig. 27.4) devised by Bunsen and Kirchhoff in 1859 consists essentially of a glass prism through which light from a flame is collected in a collimator tube (upper left in Fig. 27.4) and refracted through a prism. The spectrum so produced is viewed through a viewing telescope (upper right in Fig. 27.4). A third tube (lower centre) permits a graduated scale to be brought into the field and to be viewed along with the spectrum. By this means direct measurements of the various wave lengths which are character-



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Fig. 27.5. Spectroscopic analysis.

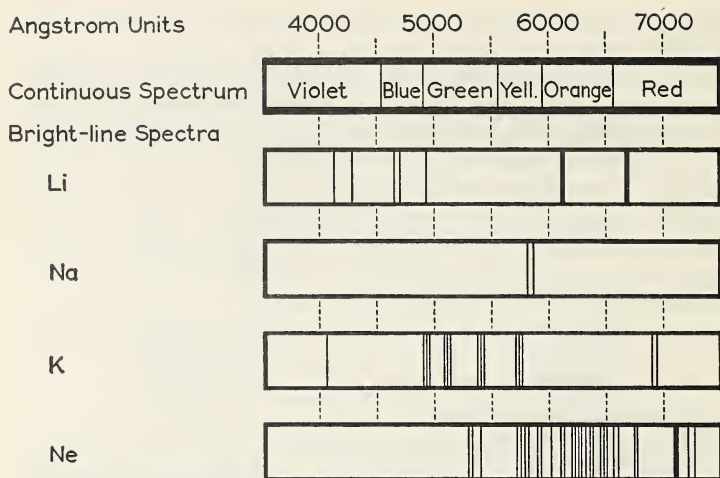


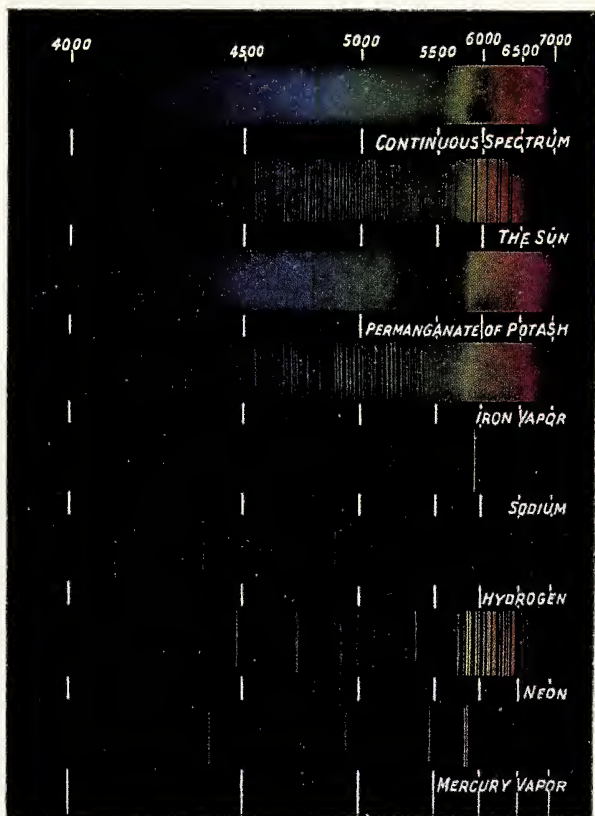
Fig. 27.6. Bright-line spectra of lithium, sodium, potassium and neon and their relationship to the continuous spectrum of the sun.

istic of the light being emitted may be made. An incandescent vapour (Fig. 27.5) or a gas glowing in an electrical charge produces a spectrum known as a bright-line spectrum (Fig. 27.6) which contains specific brightly-coloured lines characteristic of this particular vapour or gas.

Light from the sun produces a continuous spectrum composed of all the colours found in the rainbow—from red of long wave length through orange, yellow, green, blue and indigo, ending with violet, the shortest wave length which is visible.

Because the wave lengths of the various colours making up the continuous spectrum are so short, the Angstrom unit is used for their measurement. One Angstrom unit is equivalent to $\cdot 00000001$ cm. or 10^{-8} cm. If a salt of sodium is vaporized in the non-luminous Bunsen flame and the vapour observed through a spectroscope, two parallel yellow lines, very close together, appear near the 6000 Angstrom mark on the scale. These yellow lines are characteristic of sodium vapour and indicate a wave length for sodium vapour of $\cdot 000006$ cm.

Metallurgy of the metals. The activity table (p. 283) indicates that some metals are found in nature in the free or native state, i.e., they are not chemically combined with any other element. Examples of metals which may be found in the free state are platinum, gold, and in some cases, copper. More frequently, however, metals are found chemically combined with one or more other elements and in this form



SPECTRA OF VARIOUS KINDS

The first is a continuous spectrum; in it are no lines, dark or bright. In the next two are dark lines or bands, due to the absorption of different wave lengths. The last five are spectra of gases or vapours made luminous by an electric current; they show only bright lines.

The numbers at the top give the wave lengths in angstroms.

Photographs by Elizabeth J. Allin. Prints from the negatives were coloured and then reproduced.

are known as **minerals**. Examples of these minerals include hematite (Fe_2O_3), bauxite ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) (a mixture of hydrates of alumina) and chalcocite (Cu_2S).

When a mineral occurs mixed with extraneous rocky or other material the mineral is said to be contained in an **ore**. If there is a high concentration of the mineral, the production of the metal from the ore will be economically profitable. If, however, the concentration of the mineral is low, a preliminary treatment must be given to get rid of some of the extraneous material. The practical distinction between a mineral and an ore is therefore an economic one.

The process of obtaining a metal from its ores is called **metallurgy**. Certain methods of producing the pure metal have been discussed in previous chapters (see pages 241-242) while methods of producing aluminum, iron, and copper will be discussed in Chapters 28, 29 and 30. Before proceeding with a study of specific metallurgical processes, a general survey of the more common sources of metals will be made.

Metals in the free state. Platinum and gold ores usually consist of the metal in a finely-divided condition found scattered throughout the waste rocky material (gangue).

Oxides of metals. This is a common type of ore and is the starting point for iron, aluminum, and tin.

Sulphides of metals. These may be *simple* sulphides or complex compounds containing sulphur. The ores of copper, lead, mercury, zinc, cadmium, nickel, and cobalt commonly contain sulphides.

Chlorides of metals. Earlier chapters stated that sodium chloride occurs in a very pure state as the mineral **halite** which serves as a raw material for sodium. Chlorides of potassium, magnesium and calcium constitute the starting point for potassium, magnesium and calcium.

Concentration (ore-dressing). Costs of metallurgical processes are divided between the securing of the ore and the processing of the ore until the pure metal is produced. In many cases the processing costs would be prohibitive were it not for the discovery of some simple inexpensive method of separating the valuable mineral from the gangue. Any process which effectively separates mineral from gangue is known as ore-dressing or concentration and the product resulting from the process is known as the **concentrate**. There are several methods of producing a concentrate. The most common method, however, consists of grinding the ore into particles so small that each particle is either mineral or gangue, then sorting the mineral from the gangue by the froth-flotation process.

Froth-flotation. In the froth-flotation process the powdered ore, known as pulp, is fed into a flotation cell (Fig. 27.7) where small

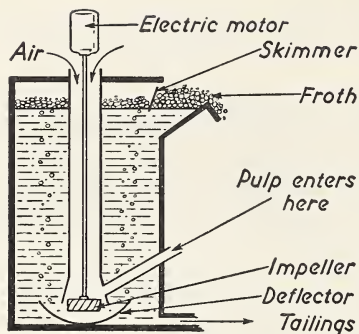


Fig. 27.7. A vertical section of a froth-flotation cell.

amounts of special oils and other chemicals are introduced. Air under pressure, accompanied by mechanical agitation, produces a froth to which the desired mineral particles adhere. The froth containing the mineral rises to the top of the open cell and is skimmed off. The enriched product, the concentrate, is collected in special tanks called launders where it is partially dried before passing to large drum-like rollers where the drying is completed. The dry con-

centrate is then transported to the refinery.

Application of the froth-flotation process to low grade copper ores from certain Canadian mines results in the recovery of as much as one ton of concentrate from six tons of ore. Without this process, separation would be economically impossible.

Metallurgical processes. There are several methods of obtaining metals from their ores. The most common are as follows:

Electrolytic processing. For those metals high in the activity series that cannot be reduced by carbon, an electrolytic method must be used to produce the metal. Sodium, potassium, calcium, magnesium and aluminum are produced by this method.

Reduction by carbon. Metals in the middle ranges of the series may be separated from their oxides by reducing them with carbon. Iron may be produced by reduction of hematite (Fe_2O_3) with carbon (p. 310).

Roasting and reduction. In some cases, especially if the ore is a sulphide, it is necessary to heat the ore in a stream of air to convert the mineral from a sulphide to an oxide. This process is known as roasting. The oxide is then reduced with carbon. The metallurgies of copper and zinc make use of this method of roasting and reduction.

Extractive metallurgy. This is a process used on low grade ores and consists of treating the ore with a leaching agent such as sulphuric acid or ammonia. By this means the metal is put into a solution from which it may be recovered later by subsequent chemical reaction.

Examples of the first three of the processes named above will be presented in the chapters that follow.

EXERCISE

A

1. State the important differences between metals and non-metals as outlined in the appendix page 374.
2. Describe one method of determining the order of activity of the metals.
3. What is meant when it is stated that iron is "more metallic" than silver?
4. Why are the active metals such as cesium and rubidium suitable for use in the photoelectric cell?
5. Explain oxidation and reduction in terms of the electron theory.
6. In the reaction $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$ which element is oxidized and which is reduced? Explain.
7. Describe how you would conduct a flame test to show the presence of barium in salt suspected of containing that element.
8. What is a spectroscope?
9. How does the continuous spectrum differ from a bright-line spectrum? How is each produced?
10. What is the purpose of "ore-dressing"?
11. Describe the froth-flotation method of treating low grade ore.
12. What is the difference between a mineral and an ore?
13. Discuss various types of minerals commonly found in ores.
14. Metallurgy is the process of obtaining metals from the ore. Discuss briefly four types of metallurgy in use today.

B

1. Devise experiments, different from any mentioned in the text, to illustrate the replacement of (i) a metal and (ii) a non-metal from a solution containing a soluble compound of each. Give ionic equations for each reaction and tell in each case which element is oxidized and which is reduced. Explain.
2. Suggest a reason why metals at the top of the activity series are never found free in nature while those at the bottom are usually found free.
3. Suppose A, B, C, D, represent four metallic elements. If strips of A, B, and C are placed in a solution of a salt of D (e.g. a chloride), A and C remain unchanged but B becomes coated with a substance whose colour resembles that of metal D; if strips A and C are placed in separate solutions of dilute hydrochloric acid, no reaction occurs with metal C but metal A liberates a gas that tests as hydrogen.
 - (a) Using the information gained from the above experiments arrange the elements in the order in which they would appear in the activity series.
 - (b) Suppose that only one of the elements will displace hydrogen from water. Name the element and give the reason for your choice.
 - (c) Insert hydrogen in its proper place in the list.
 - (d) Suppose A is placed in a solution of copper sulphate. What will happen? Explain.
4. From outside reading suggest how the spectroscope is used by the criminologist and by the astronomer.

CHAPTER 28

Aluminum

This proverb flashes through his head:
The many fail; the one succeeds.

TENNYSON

The story of aluminum is one of the most dramatic in the history of modern chemistry. A chemical curiosity in 1825, aluminum has today become a metal of vital importance.

In 1825 Hans Christian Oersted, a Danish chemist, produced aluminum by heating aluminum chloride with potassium amalgam, a solid solution formed by dissolving potassium in mercury. Two years later Freidrich Wöhler, a German chemist and a student of Berzelius (p. 118), produced aluminum in a similar fashion but used potassium metal rather than potassium amalgam. One of Wöhler's students, Frank Fanning Jewett, a chemistry professor at Oberlin College in the state of Ohio, U.S.A., remarked to his class that if anyone could invent a process to produce aluminum on a commercial scale, he would not only be a benefactor to the world, but would make a fortune. Charles Martin Hall (1863-1914), a student in the class, whispered to his classmate, "I'm going for that metal", and from that time on, discovering a cheap method of producing aluminum became an obsession with him. In attacking the problem, Hall used the scientific method (page 17) and finally, February 23, 1886, reached his goal by producing a number of small globules of aluminum.

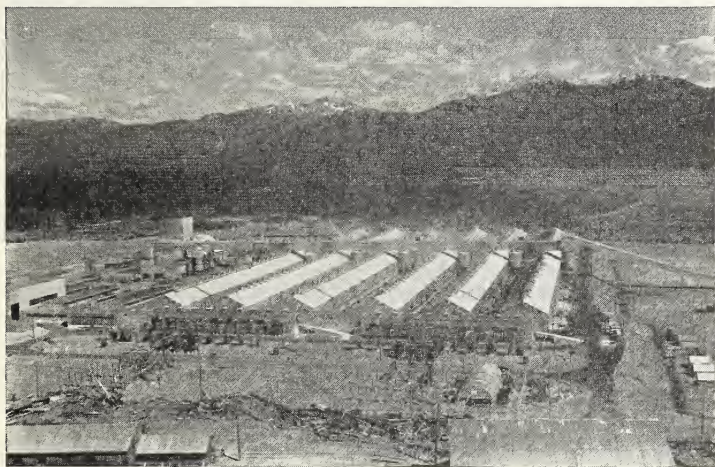
Two months after Hall's discovery, Paul Héroult (1863-1914), a French chemist, working independently, produced aluminum by the same method. In the history of chemistry there are many instances of this duplication of discovery where men, studying miles apart, make the same discovery within a short time of each other. To the first discoverer goes the credit. The others, no less deserving of recognition, merely become losers in the race.

The difficulty which Hall encountered in producing aluminum came from the fact that this metal, high in the activity series, could not be

reduced by any of the common reducing agents such as carbon. To overcome this difficulty Hall introduced the use of electric current and turned to electrolysis as his method of metallurgy. It is because of this electrochemical metallurgical process that Canada is playing an ever-increasing role in the metallurgy of aluminum.

In the year 1900 the St. Maurice River in Quebec was first harnessed for hydro-electric power and an aluminum plant was built at Shawinigan Falls. In 1925 the model city of Arvida was built around the Shipshaw aluminum plant on the Saguenay River. A third aluminum plant is now located near the Beauharnois power installation on the St. Lawrence River.

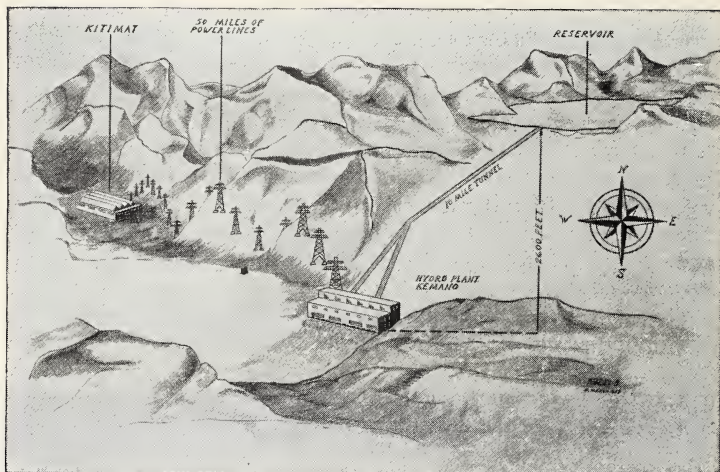
The latest development in the production of aluminum in Canada is at Kitimat in British Columbia. Some 400 miles north of Vancouver



Aluminum Company of Canada, Ltd.

Fig. 28.1. Alcan's aluminum plant at Kitimat, B.C.

the Nechako River has been dammed to provide a huge reservoir 150 miles long. This reservoir supplies water for a two million horsepower hydro plant. The water reaches the generating station by way of a ten-mile tunnel cut through solid rock. The station itself is built inside the mountain. A fifty-mile transmission line delivers the power to the smelter at Kitimat. When the project is finally in full operation, it will produce about 500,000 tons of aluminum per year, an amount greater than the present total production of all of the Canadian plants.



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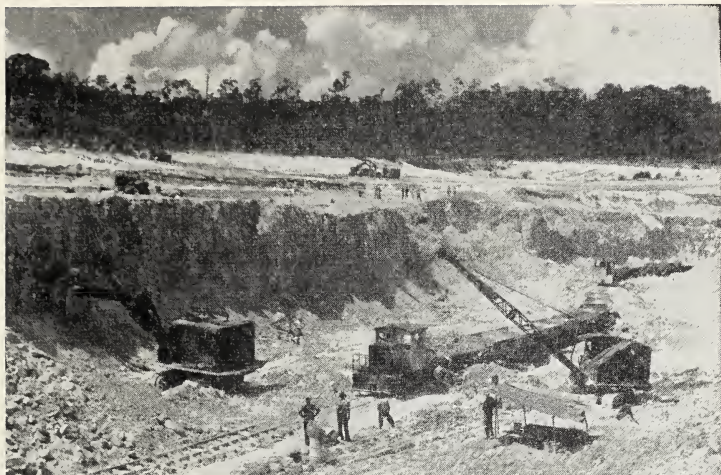
Fig. 28.2. Diagram of Alcan's Kitimat development showing power plant and smelter.

Kitimat is the newest development, but even as engineers finish this project, areas as far north as the Yukon are being surveyed as possible sites for new aluminum plants.

Metallurgy of aluminum. The ore, **bauxite** ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$), named for the village of Baux in Southern France, one of the first sources of aluminum ore, is a reddish-brown clay found in many different parts of the world. However, most of the commercial grades of bauxite are mined in areas in or near the tropics. Jamaica and British Guiana are the sources of practically all of the bauxite used in Canada.

Bauxite has a very high melting point, and one of the problems that very nearly bested Hall was the difficulty in releasing aluminum from its oxide. By experiment Hall discovered that bauxite would dissolve in **cryolite** (Na_3AlF_6), a double fluoride of sodium and aluminum ($3 \text{ NaF} \cdot \text{AlF}_3$). Cryolite is mined in Greenland and is made synthetically. It continues to be used today as the solvent for bauxite. In order to lower the melting point of the electrolyte still further, **fluorspar** (CaF_2) from Newfoundland is added to the cryolite.

Bauxite must be purified before it can be used in the electrolytic cell. To bring about the purification, the bauxite is dissolved in concentrated sodium hydroxide solution. The resulting solution is filtered and when diluted with water pure aluminum hydroxide precipitates, which



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Fig. 28.3. Mining bauxite in British Guiana.

on heating produces nearly 100% pure alumina (Al_2O_3). This pure Al_2O_3 is then fed into the reduction furnace or electrolytic cell called the *pot* in the trade, where it dissolves in the molten mixture of cryolite and fluorspar.

The reduction furnace (Fig. 28.4) usually about 10 feet wide and 16

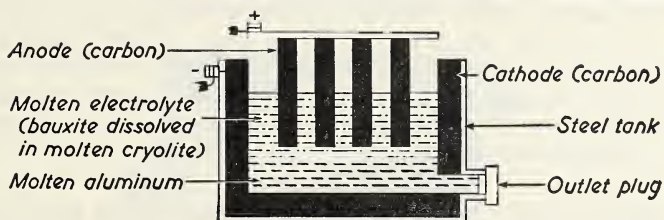


Fig. 28.4. Hall's electrolytic reduction process. In addition to the molten cryolite and alumina, the cell contains fused fluorspar which acts to produce a lower melting point for the solvent.

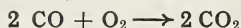
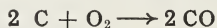
feet long consists of a steel shell lined with a paste of coke which is baked until hard. This lining forms the cathode of the cell. The anode of the cell consists of carbon blocks. Reduction furnaces are also known as electrolytic cells and a single plant, for example Arvida, Quebec, may contain as many as 2,500 of these units.

The electrical circuit is closed by lowering the carbon anode to the cathode lining and then raising the anode. The powerful arc which is struck produces sufficient heat ($1000^{\circ}\text{C}.$) to keep the electrolyte molten. The reaction at the cathode may be represented by the equation



The molten metal sinks to the bottom of the cell and is tapped off and cast into **ingots** which may weigh as much as 1000 pounds. The ingots are shipped to plants for finishing into the various products made from the metal.

Oxygen liberated at the anode unites with the carbon forming carbon monoxide which in turn may burn to form carbon dioxide.



Hall's electrolytic process is continuous. Alumina must be added from time to time and the carbon blocks of the anode replaced as needed. The cryolite and the fluorspar, however, are not consumed. Because the alumina which is placed in the cell is almost 100% pure, aluminum metal which is better than 99% pure is produced by the process.

Physical properties. Aluminum is one of the lightest of the common metals (sp. gr. 2.7) and is silvery white in colour. Aluminum is malleable and ductile and can be cast, rolled, forged, extruded and drawn. It is a good conductor of heat and of electricity. The pure element melts at $660^{\circ}\text{C}.$, and boils at $1800^{\circ}\text{C}.$

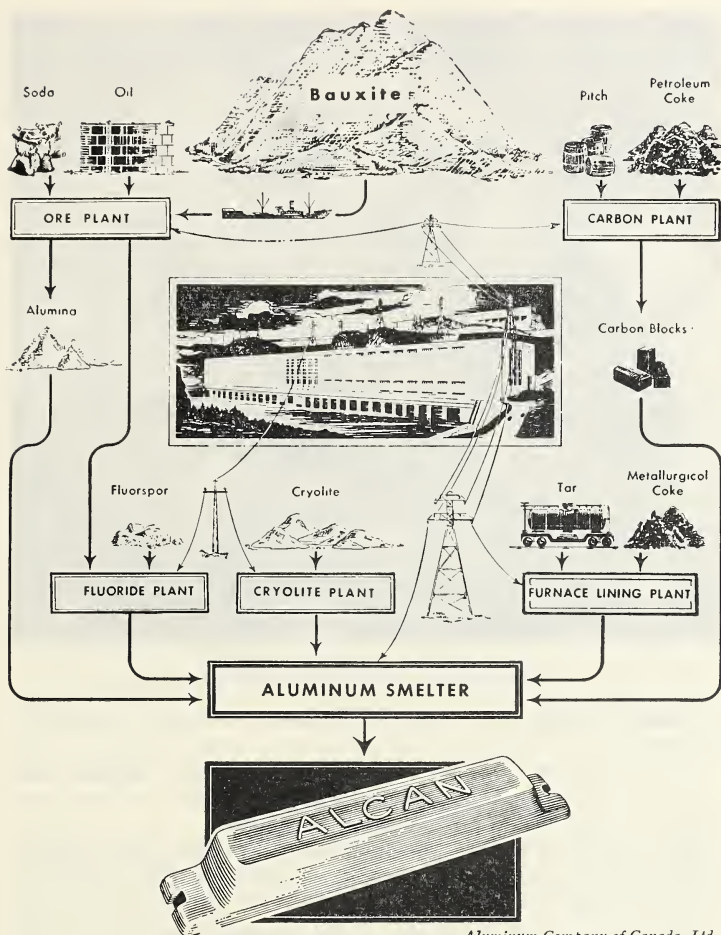
Chemical properties. Aluminum is a fairly active metal, as shown by its position in the activity series (p. 283). A fresh aluminum surface becomes coated with a very thin oxide film. However, this oxide film effectively prevents further oxidation by oxygen in the air. Thus, aluminum metal and many of its alloys can be used without the progressive deterioration that occurs with iron.

USES OF ALUMINUM

Kitchen utensils. Because of its lightness and its good heat conductivity one of the first uses of aluminum was in the manufacture of kitchen utensils.

In the building trades. Because of the lightness of aluminum and the fact that it forms a protective coating of aluminum oxide (Al_2O_3) that adheres closely to the surface of the metal, it is used extensively in the building trades. In addition to flashings and sidings on buildings, aluminum is also used in the manufacture of window sashes and doors.

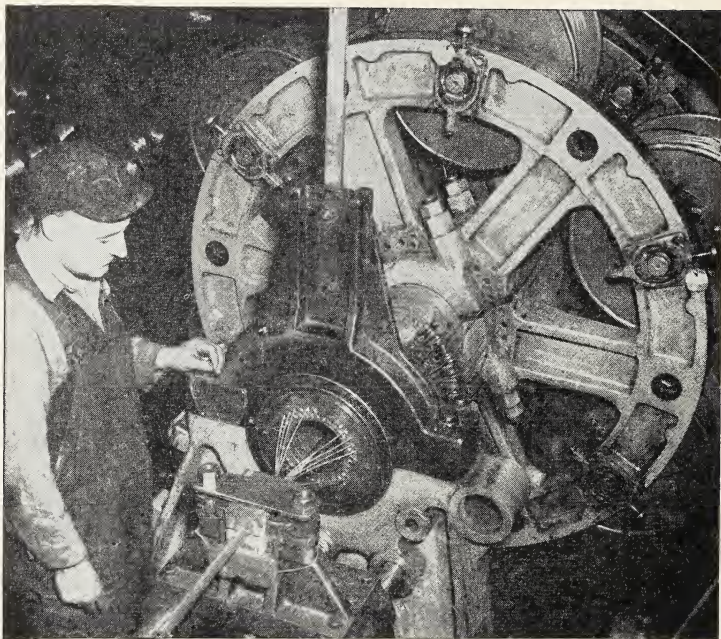
In the electrical industry. Aluminum is useful in high tension lines



Aluminum Company of Canada, Ltd.

Fig. 28.5. The aluminum ingot. It takes about 7 tons of raw materials, plus electrical energy equivalent to 16 tons of coal to make 1 ton of aluminum.

because of its lightness and high electrical conductivity. A great portion of the cost of power lines is in the construction of the supporting towers. Because aluminum is lighter than copper, transmission cables made from aluminum require fewer towers for support, and costs are greatly reduced. The aluminum conducting cables are made



Aluminum Company of Canada, Ltd.

Fig. 28.6. Stranding aluminum cable at Alcan's Shawinigan Falls works.

by lacing aluminum wires around a steel core which gives strength to the cable.

In transportation. The use of aluminum and certain of its alloys for airplane, automobile, and railroad parts now takes more than one-third of the total world production of the metal.

In the making of alloys. Aluminum is of great value today because of the considerable number of alloys that may be produced using it as a starting point.

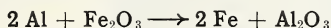
The art of alloying was known to the ancients who mixed varying quantities of other substances with a metal and thus changed the original nature of the metal. Bronze is an example of an alloy produced by the ancient art.

Aluminum metal is comparatively soft and a one-inch test bar breaks under a load of 15,000 pounds. However, aluminum alloys can be produced so strong that a similar test bar will lift a load of 80,000 pounds. A summary of the more common alloys is given in the following table:

COMMON ALUMINUM ALLOYS

NAME	COMPOSITION	PROPERTIES	USES
Duralumin	Al; Cu; Mn; Mg	Lightness of aluminum with strength of steel	Airplane engines and parts
Magnalium	Al; Mg	Lightness	Suitable for machining
Aluminum- bronze	Al; Cu	Great tensile strength; easily cast	Crankcases, connecting rods, other motor parts
Alclad	Duralumin coated with pure aluminum	Resistant to corrosion, especially sea water and atmosphere	Yacht masts, airplanes, railway cars
Alnico	Fe; Al; Ni; Cu	Light, highly magnetic	Light permanent magnets of great strength, radio and TV speakers

The thermit process. Aluminum is above iron in the activity series. A mixture of powdered aluminum and ferric oxide (Fe_2O_3) when ignited by burning magnesium ribbon produces molten iron.



An enormous amount of heat is produced by this reaction and for this reason it is called the thermit process. The process has practical use for welding broken castings which cannot readily be removed from their position.

ALUMINUM COMPOUNDS

Aluminum, although too active to occur as the free metal in nature, is widely distributed as the oxide (Al_2O_3), either hydrated or unhydrated, and either uncombined or combined with other compounds such as silica (SiO_2).

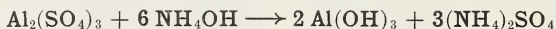
Aluminum is in Group III of the Periodic Classification. Thus it has a **valence of three** in its compounds. It forms **white** compounds.

Aluminum oxide or alumina (Al_2O_3). Aluminum oxide occurs in nature as **corundum**, and when contaminated with iron oxide is called **emery**. The gems **ruby** (red) and **sapphire** (blue) are coloured crystalline aluminas.

Industrially, aluminum oxide is made by fusing precipitated aluminum hydroxide in an electric furnace. The oxide is very hard

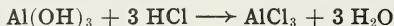
and has an exceedingly high melting point. For these two reasons, the oxide is important as an abrasive in grinding wheels and as electric furnace lining.

Aluminum hydroxide $[\text{Al}(\text{OH})_3]$ can be prepared by adding ammonium hydroxide to a solution of an aluminum salt.

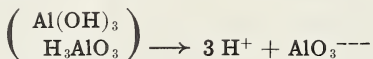


The aluminum hydroxide forms a white gelatinous precipitate.

Aluminum hydroxide exhibits the property of **amphoterism**, that is, it behaves as an acid in the presence of a strong base and as a base in the presence of a strong acid. When in the presence of a strong acid, aluminum hydroxide dissociates to form aluminum ions and hydroxyl ions, and the hydrogen ions of the acid unite with the hydroxyl ions of the base to form water.



When in the presence of a strong base, the aluminum hydroxide $[\text{Al}(\text{OH})_3]$ dissociates as if it were a compound having the formula H_3AlO_3 . The H_3AlO_3 ionizes forming hydrogen ions and aluminate ions.



The hydroxyl ions of the base unite with the hydrogen ions of the acid to form water.



The ability of aluminum hydroxide to act either as an acid or as a base is indicated by the position of aluminum in the Periodic Table (p. 238). Aluminum follows the distinctly metallic element magnesium and comes before the non-metal silicon. It is not surprising therefore that aluminum may act chemically both as a metal and as a non-metal (Appendix E).

The addition of a very small amount of sodium hydroxide to a solution of an aluminum salt produces a white gelatinous precipitate of aluminum hydroxide.



The addition of excess sodium hydroxide, however, causes the precipitate to dissolve forming sodium aluminate, which is soluble in water.



Aluminum hydroxide as a gelatinous precipitate is used to remove suspended matter from city and town water supplies. The aluminum

hydroxide removes the turbidity from the water but does not remove harmful micro-organisms. Water must be chlorinated (p. 224) to make it safe for drinking.

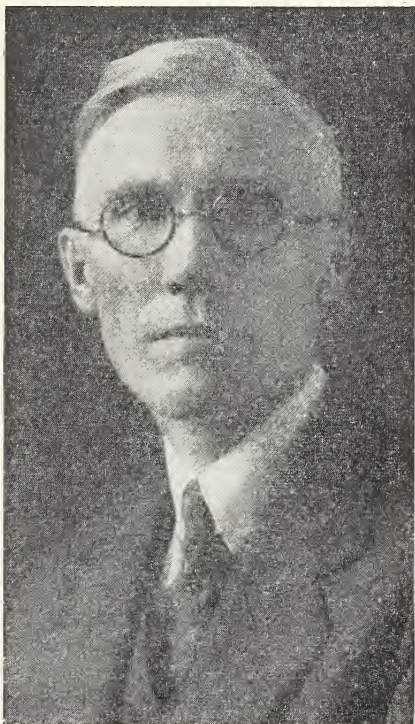
Aluminum hydroxide is also used as a **mordant** in the dyeing of fabrics. Fabrics to be dyed are dipped into an alum solution [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$], then treated with a very weakly alkaline solution to precipitate the aluminum hydroxide both *inside* and *outside* the fabric. The fabric is then immersed in the dye-bath. The dye and the aluminum hydroxide form an insoluble coloured substance known as a "lake", and in this way the aluminum hydroxide binds the dye to the cloth.

Anhydrous **aluminum chloride** ($AlCl_3$) is an important catalyst in organic chemical reactions.

Aluminum fluoride (AlF_3) with sodium fluoride has a strong tendency to form the complex salt, cryolite (Na_3AlF_6). Molten cryolite is the solvent for alumina in the electrolytic production of aluminum (Hall-Héroult process).

Potassium alum [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$] has been known for a very long time as potassium alum, or common alum. It is a member of a series of related hydrated double sulphates. Sodium or potassium alum is used as the acid-forming ingredient in some baking powders (p. 178) and in fire extinguisher mixtures (p. 176).

The simple **aluminates**, sodium and potassium aluminate, are soluble in water (see above). Calcium aluminate is insoluble in water and is an essential component of Portland cement.



William Notman & Son Ltd.

Fig. 28.7. Dr. Thorbergur Thorvaldson.

Portland cement is made by heating a mixture of limestone (CaCO_3) and clay (alumina silicates) to a high temperature. The resulting clinker containing calcium aluminate and calcium silicates is ground and bagged. The hardening of Portland cement in a wet mortar is largely due to the hydration of the aluminate and silicates, e.g. $(3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSiO}_3 \cdot 12 \text{ H}_2\text{O})$.

In western Canada large areas of soil—so-called “alkali” sloughs—are contaminated with salts of sodium and magnesium chiefly as sulphates. Portland cement concrete slowly disintegrates in these soils.

Dr. Thorbergur Thorvaldson at the University of Saskatchewan discovered a way to make Portland cement resistant to sulphate action. Thorvaldson added iron oxide to the raw material used in the manufacture of Portland cement; this converted the sulphate-vulnerable calcium aluminate to the unreactive calcium alumina ferrite. This sulphate-resistant cement is accepted as the standard in both the United States and Canada.

EXERCISE

A

1. How was aluminum produced prior to 1886?
2. Why is it necessary to use an electrolytic method to produce aluminum from its oxide?
3. Discuss Canada's role in the production of aluminum.
4. Where is the bauxite obtained that is used in Canada's aluminum plants?
5. (a) Why does Hall's process for making aluminum require a great amount of petroleum coke? (b) What is the function of the cryolite and the fluorspar in the process? (c) How is the ore concentrated and purified? (d) What reaction takes place at the cathode? (e) Why must the carbon anodes be replaced?
6. What properties of aluminum make it useful in (a) the kitchen, (b) the building trades, (c) the electrical industry, (d) modern transportation?
7. What is an alloy?
8. Name the more important alloys of aluminum and give the properties which make these alloys useful.
9. Explain why a mixture of iron and aluminum oxide does not give a chemical reaction.
10. Why is aluminum metal never found in the pure state in nature?
11. Describe the property of amphoterism as applied to aluminum hydroxide.
12. Why does aluminum behave both as a metal and as a non-metal?
13. In what way is aluminum similar to and in what way is it different from (i) the alkali metals and (ii) the alkaline earth metals?
14. Aluminum is higher in the activity series than iron, yet while iron rusts and corrodes, aluminum withstands the action of the atmosphere. Explain.
15. When excess ammonium hydroxide is added to an aluminum salt, a precipitate of aluminum hydroxide results. When excess sodium hydroxide is added to an aluminum salt, no precipitate remains. Explain.
16. What are the uses of (a) aluminum hydroxide, (b) potassium alum?
17. What is Portland cement? What is the composition of cement mortar after it has set?

CHAPTER 29

Iron and Steel

And he sang: "Hurrah for my handiwork!"
And the red sparks lit the air;
"Not alone for the blade was the
bright steel made,"
And he fashioned the first ploughshare.

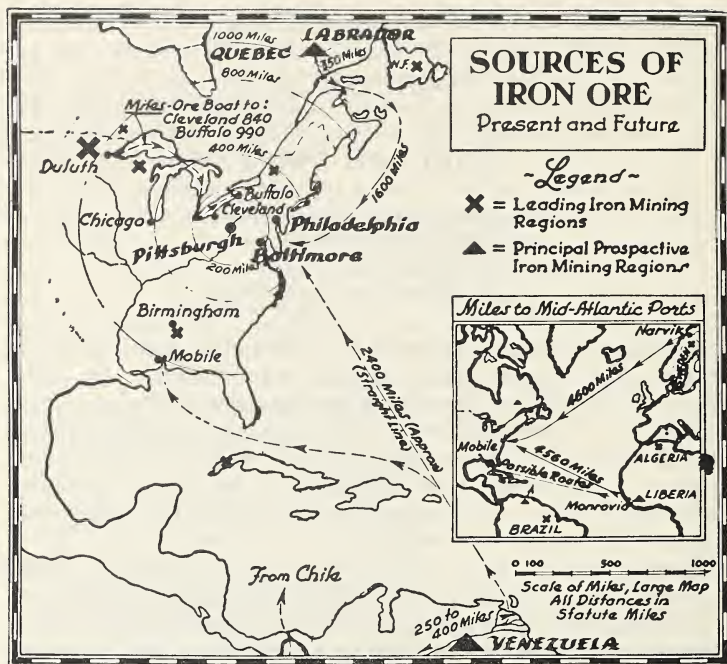
CHARLES MACKAY

Iron has been serving man for the past 5000 years. Iron implements which date back to this time have been found in Egypt. No doubt the early metallurgy of iron resulted from the chance building of huge campfires on outcroppings of the ore, and the iron produced was undoubtedly of very poor quality. Because of the work of the scientist, however, improvements have been made in metallurgical processes until to-day steel, an alloy of iron, is without doubt the world's most important metal-like substance.

The ores of iron. Iron is seldom found in the free condition. While meteorites are practically pure iron mixed with some nickel, they are so rare that they are considered as scientific curiosities rather than as sources of iron. Ores of iron which are found in the form of oxides are **hematite** (Fe_2O_3), **magnetite** (Fe_3O_4), and **limonite** ($2 \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$). Another ore known as **siderite** occurs as the carbonate (FeCO_3).

Deposits of iron ores are widely distributed on the earth. France, Germany and Russia all have extensive deposits of the oxides, and Great Britain produces considerable quantities of siderite. The Mesabi Range, southwest of Lake Superior, supplies a vast amount of hematite for the United States. Recently Venezuela has become an important exporter of iron ore.

Although a small amount of iron ore has been produced in Newfoundland, Canada's steel industry has been largely dependent for many years upon iron ore imported from the United States. The necessity of importing hematite from the United States arose from the fact that until recently Canada had little knowledge of her rich resources of iron ores. In 1890 Dr. W. H. C. Smith, a geologist, reported a deposit of high-grade iron ore along the south shore of Steep Rock Lake, approximately 150 miles west of Port Arthur, Ontario. An attempt was made to mine the ore, but the inaccessibility of the region caused the operation to be abandoned in 1903.



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Fig. 29.1. Map showing actual and potential sources of iron ore.

In 1937, Julian Cross, a mining engineer, using a diamond drill (see pages 165-7) and working through the ice in winter, prospected the bottom of Steep Rock Lake. His findings indicated a large body of ore of very high grade. Before it could be mined, however, the course of a river had to be diverted, the inlet to the lake had to be dammed, and the lake itself had to be drained.

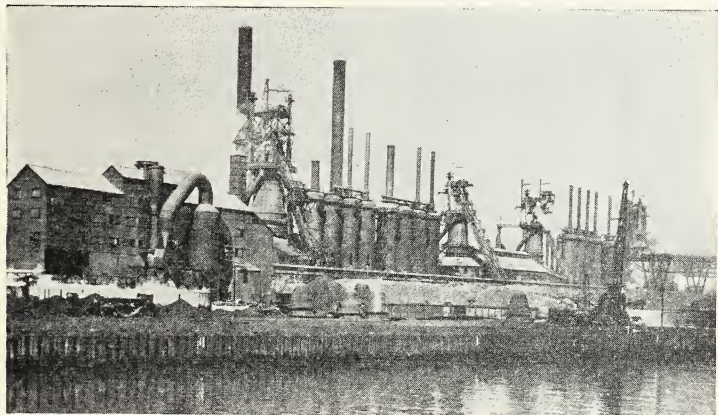
To-day three open-pit mines are located side by side on what was once the bottom of the lake, and underground work has already been started. In the first three years of operation 3,000,000 tons of ore have been removed and reserves of hematite that are possibly in excess of one billion tons have been discovered.

As early as 1894, A. P. Low, a government geologist, told of great deposits of iron ore in the Ungava region of northern Quebec and Labrador. Because of inaccessibility and other difficulties there was little or no attempt made to develop the deposits at that time. The advent of

World War II, however, brought with it greatly increased demands for more iron and steel. The steel industry felt that the Mesabi Range was insufficient and even showed signs of running out. By the early 1940's interest in the Ungava project was revived and plans were laid to overcome the difficulties involved in building railroads, developing power sites, tunnelling through mountains and building bridges over deep chasms. The planners realized that at least \$200,000,000.00 would be required for the project, but they also realized that the inexhaustible supply of iron ore in this area would eventually more than repay the initial cost and would make Canada one of the richest sources of iron in the world.

Metallurgy of iron. Almost invariably iron ore (hematite) is reduced to the metal in a **blast furnace**. Carbon in the form of coke burns to carbon monoxide which acts as the reducing agent. The blast furnace is sometimes called a **smelting furnace** because the metal is obtained from the ores by a process of melting or fusion.

The blast furnace. The blast furnace is a cylindrical structure 80 to 125 feet high, constructed of steel plates and lined with a thick layer of some refractory material (silica or magnesia). The charge consisting of hematite ore, limestone and coke is introduced through a hopper at the top of the furnace, and the molten iron is withdrawn from the crucible at the bottom of the furnace. The production of each ton of iron requires 1.5 tons of hematite ore, 1 ton of coke, 0.5 ton of limestone, and nearly 4 tons of air.



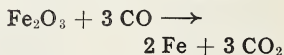
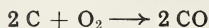
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Fig. 29.2. Ore dock and blast furnaces. At left is the sinter plant where fine iron ore and flue dust are sintered for recharging into the blast furnace.

The limestone is added to act as a **flux** which unites with the rocky impurities in the ore to form a **fusible slag**. The charge carried up to the hopper by "skip cars" falls into the furnace in alternating layers.

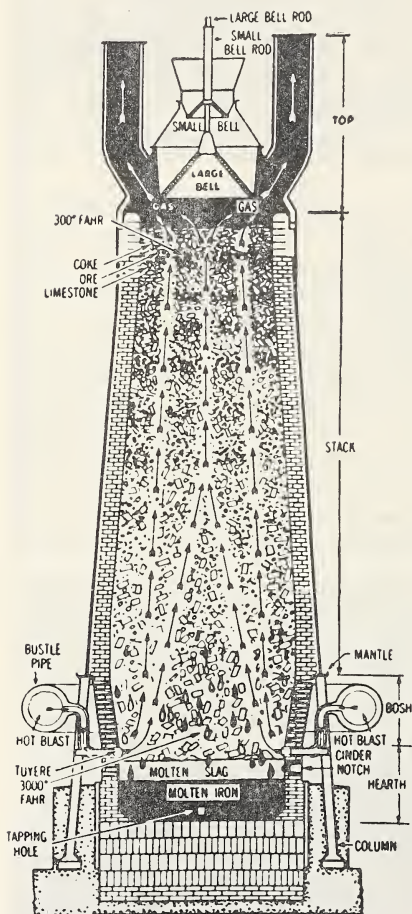
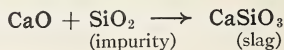
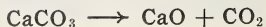
Air is heated to a temperature in excess of 1200°F . by a series of large stoves adjacent to the main furnace and using blast furnace gases as fuel. The air is introduced through **tuyeres** near the bottom of the stack. When the furnace is "in blast" the temperature at the top is about 300°F . while at the bottom of the stack it is close to 3000°F .

As the charge descends through the areas of increasingly higher temperatures, carbon monoxide formed by incomplete combustion of the coke reduces the hematite to iron and the carbon monoxide is oxidized to carbon dioxide.



The reduction of the hematite by the carbon monoxide takes place largely in the top half of the furnace.

About half way down the stack the limestone begins to react with the rocky impurities to form a fusible slag.



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Fig. 29.3. Diagram of a blast furnace. Coke, limestone and iron ore are dumped into the top of the furnace in alternate layers. Hot air is blown in near the bottom. Pig iron and slag are tapped at the base.

As the charge descends further it enters the **zone of fusion** where the mixture becomes a pasty mass. Still lower in the stack, where the temperature is higher, the iron and the slag become liquids. In this area the ash from the burned coke is absorbed by the liquid slag. The iron absorbs silicon from the slag and carbon from the coke. Both the iron and the slag are in a molten state and drop to the hearth where the slag, less dense than the molten iron, floats on top of the iron. About every four or five hours the slag is tapped off through the **cinder notch**. The iron is drawn off through the **tapping hole** which remains sealed with a fire-clay plug until the iron is ready to be removed.

From this description of the operation of the furnace it is obvious that once a furnace has been fired the operation is continuous as long as the refractory firebrick lining remains intact. The modern blast furnace is capable of producing 500 to 1000 tons of iron during each 24-hour period.

If the iron is to be processed further, it is poured into **hot-metal cars** which have a capacity of 40 to 160 tons. These cars are so constructed that they can deliver the iron in a molten state to the steel mills for further treatment. Upon arrival at the mill the molten iron is emptied into a **mixer** in preparation for the next process.

The molten iron may be cast into steel molds and allowed to harden. The masses of hardened iron from these molds are known as **pigs**, and the iron from the blast furnace is known as **pig-iron**. Pig-iron is quite impure and is used to make either cast iron, wrought iron or steel but the great bulk is used for the manufacture of **steel**. Pig-iron contains from $3\frac{1}{2}\%$ to $4\frac{1}{2}\%$ of carbon which makes it hard and brittle. Other impurities present in pig-iron are compounds of phosphorus, sulphur, silicon and manganese. The presence of sulphur makes iron brittle when it is hot, whereas phosphorus makes it brittle when it is cold.

Cast iron is produced by heating molten pig-iron with scrap iron which removes some of the impurities present in the pig-iron. **Wrought iron** is obtained by removing most of the impurities from pig-iron by heating in a specially-constructed furnace known as a reverberatory furnace. Wrought iron is relatively soft but is tough and can be readily welded. It is useful in making articles such as chains, anchors and bolts, which must withstand sudden stresses.

The blast furnace is one of the most efficient chemical plants known. The iron produced in it can be used in foundries or as a starting point in the manufacture of steel. The slag also is valuable in the making of cement and insulating materials. Blast furnace gases are piped to the stoves which preheat more air for the process.

The making of steel. Steel is an alloy of iron containing less than 1.5% carbon. An **alloy** is a mixture or a solid solution composed of a metal and one or more other elements mixed in the molten state to produce a substance having metal-like characteristics. Steel may be made either by the Bessemer process, the open-hearth process, or by the electric furnace method.

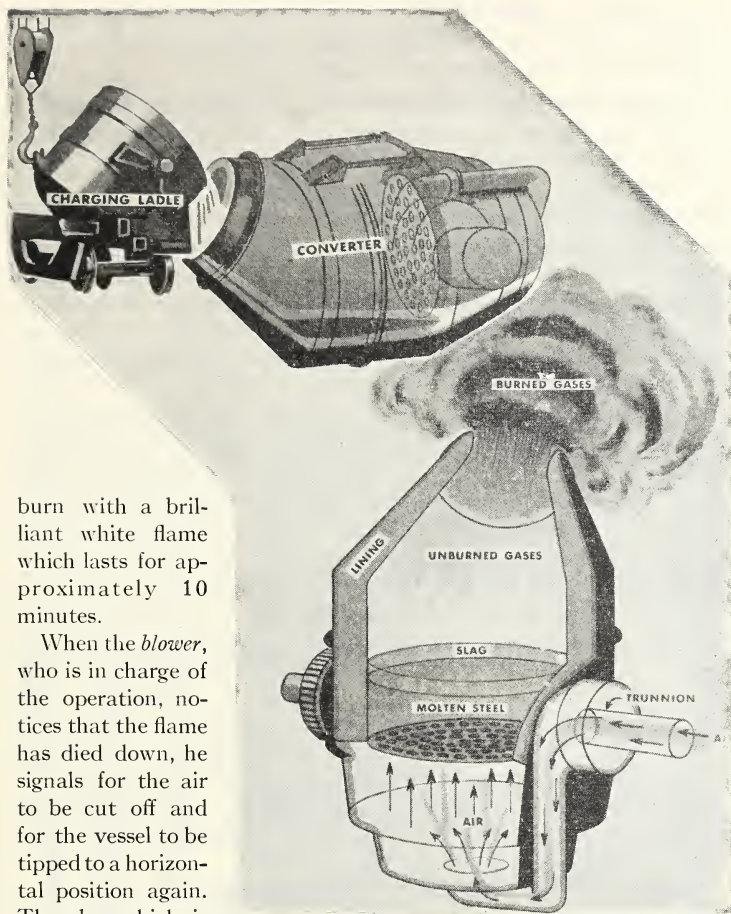
The Bessemer process. Prior to 1856 the making of steel from pig-iron was a slow and expensive process. The steel produced was not always uniform and therefore not suitable for the purpose for which it was intended, with the result that the alloy was used in limited quantities. Bessemer in England and Kelly in the United States, working independently, developed a process in 1856 that revolutionized the steel industry. This process is known to-day as the Bessemer process.

The basic reason for the success of the Bessemer process is that silicon, manganese and carbon, at the temperature of molten iron, 1535°C., will burn when exposed to a blast of air. The heat given off by the oxidation of these impurities is sufficient to raise the temperature of the contents above the melting point of iron. The Bessemer process made it possible for steel to be produced cheaply enough for general use.

The Bessemer process takes place in a Bessemer converter (Fig. 29.4). The converter is a pear-shaped vessel made of heavy steel plates and lined with heat-resistant bricks which are usually made from silica (SiO_2) an acidic anhydride, and fire clay. The converter is mounted on a horizontal axle which permits easy tilting for filling, and the bottom is full of holes through which compressed air is blown, immediately after the charge has been added. The average converter has a capacity of from 15 to 25 tons and is so constructed that a charge of molten pig-iron may be brought from the "mixer" and poured directly into it while the converter is held in a horizontal position. The blast of air is then turned on with an air pressure of 22 to 28 pounds per square inch, and the vessel is gradually raised to a vertical position.

The reaction with the air blast is immediate and violent. The silicon impurities oxidize and together with some ferrous oxide that has been formed by the oxidation of some of the iron produce a slag of ferrous silicate (FeSiO_3). During this period (approximately 5 minutes for a 25-ton charge) a yellow flame comes from the mouth of the converter.

By the time the silicon impurities have been burned out, the carbon starts to oxidize. This combustion produces great volumes of gases which come from the mouth of the converter with a great roar and



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Fig. 29.4. Diagram of a Bessemer converter.

burn with a brilliant white flame which lasts for approximately 10 minutes.

When the *blower*, who is in charge of the operation, notices that the flame has died down, he signals for the air to be cut off and for the vessel to be tipped to a horizontal position again. The slag which is floating on top of the molten iron

runs off first, leaving practically pure iron which is poured into ladles. This molten iron has a low percentage of carbon and contains dissolved gases. To produce steel of known composition a definite amount of an alloy of predetermined composition is added to the molten metal in the ladle. If small amounts of manganese are required, the alloy **spiegeleisen**, which contains 15 to 30% manganese and 4.5

to 5% carbon, is used. If the steel requires a high percentage of manganese, the alloy **ferromanganese**, which contains 78 to 82% manganese and 6 to 7% carbon, is used.

Uses and limitations of Bessemer steel. The chief uses of Bessemer steel include the making of sheet steel, pipes, bars, and rails. Because this type of steel contains some sulphur it cuts without "balling" under the blade of a cutting tool.

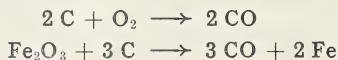
Only a small percentage of the steel produced to-day comes from the Bessemer process. Bessemer steel is not flexible enough to be entirely satisfactory for construction purposes. Furthermore, much of our iron ore contains compounds of phosphorus and as these and other acid-acting impurities are not removed by the Bessemer process, the quality of Bessemer steel is somewhat inferior to steel produced by the open-hearth process.

The open-hearth process. Ninety percent of all the steel used to-day is produced in the open-hearth furnace. The furnace itself is a large, completely enclosed rectangular brick structure (Fig. 29.5). The name "open-hearth" is used because the shallow, basin-like floor of the furnace, where the charge is placed, is exposed to the flames produced by the burning of natural or manufactured gas, oil, or of a combination of gas and oil. To promote complete combustion of the fuel, air is introduced under pressure. The fuel and the air are both preheated, and the operating temperature reached by the furnace is close to 1700°C. As the materials placed in the open-hearth furnace are usually acidic because they contain phosphorus, the lining of the furnace is made up of bricks of magnesia (MgO) and of lime (CaO).

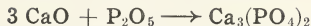
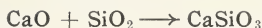
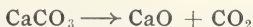
The charge is controlled by the *melter* who is responsible for the furnace. Each charge varies, depending upon the type of steel required, but it usually contains varying amounts of **molten pig-iron, a mixture of iron ore and rusty scrap steel, and limestone**, which acts as the flux in slag formation.

Undesirable substances in the pig-iron usually include carbon, silicon, phosphorus and sulphur. These are removed during the process as indicated by the following reactions:

(i) The carbon is burned out by the oxygen of the air and by the action of the iron oxide.



(ii) Calcium oxide formed by the heating of the limestone flux reacts with the silicon and phosphorus impurities to form a fusible slag.

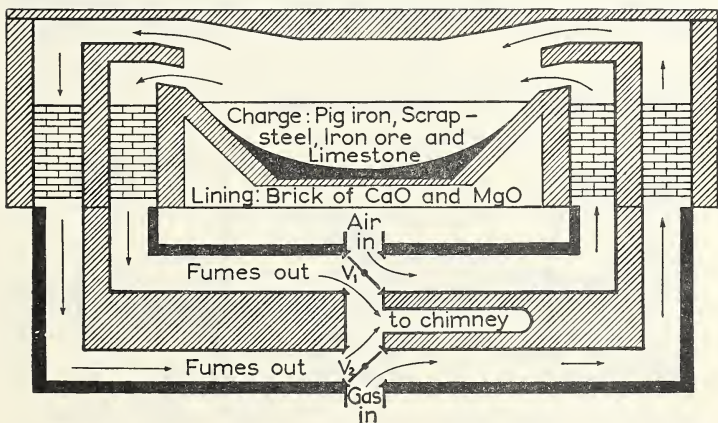


Iron sulphide reacts with the ferrous oxide that has been formed by oxidation of the iron and produces sulphur dioxide which escapes as a gas.



The hot products of the combustion of these impurities, along with the gases resulting from the combustion of the fuel, escape through ports at one end of the furnace, and pass through a checkerboard of bricks called regenerators. When the heat has been removed, the gases are then vented to the atmosphere through a stack. While the regenerators at the exit port are being heated by the exhaust gases, those at the entrance are giving up heat to the fuel which is being preheated. The flow of the mixture of fuel and air is reversed at approximately twenty-minute intervals, and in this way the process utilizes heat that would otherwise be wasted and assures a constant supply of heat to preheat the mixture of air and fuel. The direction of flow is controlled by the valves V_1 and V_2 as shown in the diagram of the furnace, Fig. 29.5.

The time required to process 100 tons of steel averages $11\frac{1}{2}$ hours. As the "heat" nears the completion time, samples are taken frequently



American Iron and Steel Institute

Fig. 29.5. Diagram of open-hearth furnace. Incoming air and gas are preheated in the brickwork checker chambers. The hearth of the furnace is open to flames which melt the charge.

and quickly analysed. If the analysis shows that a change in composition of the steel is required, suitable additions are made to the heat.

When the *melter* is satisfied that the steel is of the correct composition and that the process is complete, the furnace is tapped. The slag, which now carries the impurities, is less dense than the steel and floats on the surface from which it is skimmed off. Either spiegeleisen or ferromanganese is added and the steel is *teemed* (poured) into ingot molds.

Uses of open-hearth steel. Open-hearth steel is used for rails, machinery, structural work, and ship-building.

The electric furnace. Electric furnace steel is obtained by refining steel which has been produced by the Bessemer and open-hearth furnaces in either electric arc or electric induction furnaces. In the arc furnace the molten steel contained in a large crucible is heated by a current of electricity flowing through the steel between carbon electrodes. In the induction furnace the heat is generated within the molten metal by placing the crucible inside a coil through which an alternating current of high frequency is passed. Electric furnace steel is used for the production of high-grade products and specialized alloys. The capacity of each electric furnace is approximately 500 pounds. The steel contained in the ingots is processed in a variety of ways, depending upon the uses to which the steel will be put.

Rolling. Steel is relatively plastic at 875°C . and may be rolled into thin sheets at this temperature. It is important that the rolling be

FLOW CHART OF STEELMAKING

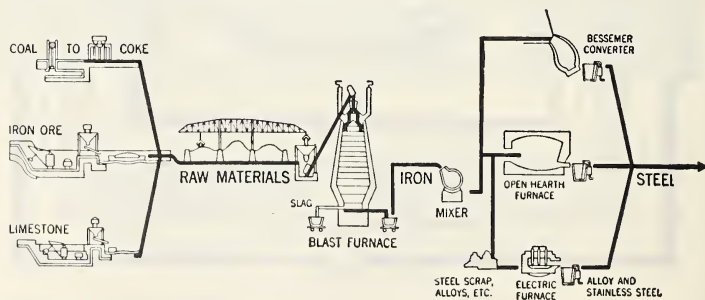


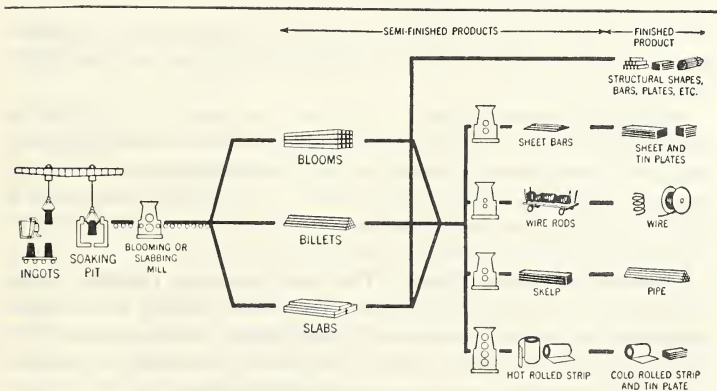
Fig. 29.6. Flow chart of steelmaking.

carried out gradually so that the steel will not rupture externally or internally. To accomplish this gradual change in thickness, the metal makes a series of *passes* through the various rollers of the mill. Since the correct temperature must be maintained, the ingot molds are transferred to a "soaking pit" where they are brought to a temperature of 1300°C . By thus raising the temperature, sufficient heat is assured for the complete rolling process.

Tempering. When steel is heated to a specific high temperature, **quenched** (cooled quickly), reheated to a specific temperature, and then cooled under control, the steel is said to be tempered. If hot steel is cooled slowly, it becomes soft and tough, but if it is quenched with cold water, it will be hard and brittle. The toughness and the hardness of the steel can be controlled by careful regulation of this tempering process.

Case-hardening. Soft, tough steel may be **carburized**, or case-hardened, by heating it in contact with charcoal. The carburizing forms an outside layer of steel which contains a high percentage of carbon. Accordingly the outside of a carburized object is hard while the centre remains soft and tough. A similar result may be obtained by a process known as **nitriding**, where the steel is heated in an atmosphere of ammonia.

Alloy steels. Alloy steels are produced when other elements in addition to carbon are added to the molten steel. Alloy steels have many desirable properties not found in ordinary steel and because of these properties have a multiplicity of uses.



Some of the more important alloy steels are tabulated below.

SOME ALLOY STEELS

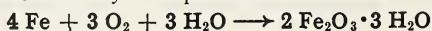
NAME OF STEEL	COMPOSITION	OUTSTANDING PROPERTIES	USES
Manganese	10-14% Mn	Hard and tough	Rock crushers, bank vaults, tractor cleats, power shovels
Tungsten	4-18% W	Retains temper when hot	High-speed cutting tools
Nickel-chromium	1-4% Ni 0.5-2% Cr	Hard, high tensile strength	Armour plate
Nickel-chromium	8-20% Ni 10-20% Cr	Rust proof at ordinary temperatures	Stainless steel
Invar	36% Ni	Low coefficient of expansion	Pendulum rods, measuring units
Silicon (Duriron)	12-14% Si	Resists action of acids	Chemical equipment for distilling acids

Uses of steel. Railroads are among the greatest users of steel both for rails and equipment. Steel is also used in great amounts for the building of ships, bridges, automobiles, and the manufacture of hardware. The framework of large buildings is usually made of steel. The petroleum industry and the mining industry make extensive use of the various alloy steels.

Much steel is used as the basic form for the manufacture of stamped goods. The so-called "tin can" is made of soft steel covered with a thin plating of tin.

Physical properties of iron. Pure iron is not made on a commercial scale but it may be prepared for scientific research work by reducing hot ferric oxide with hydrogen or by the electrolysis of a ferrous sulphate solution using iron electrodes. In the pure state, iron is silvery-white, ductile, malleable, and fairly soft. It melts at 1535°C. and has a density of 7.87 gm. per cc.

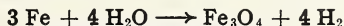
Chemical properties of iron. The most important reaction of iron is the action that takes place when iron rusts. Rusting is a complex process requiring the presence of both oxygen and moisture. Iron does not rust in dry air but it does rust in the presence of oxygen and water. The reaction may be represented as follows:



The film of rust is quite porous and does not adhere closely to the surface of the metal as do the oxides of aluminum and copper. Hence it does not protect the iron from further rusting. The corrosion of iron constitutes a very serious problem in industry and results in heavy financial loss. Some of the methods of reducing the corrosion of iron are:

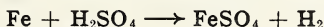
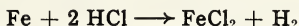
1. Coating the iron with other metals (e.g. galvanized iron has a coating of zinc).
2. Adding corrosion inhibitors to fluids in contact with iron (e.g. anti-freeze additives to reduce radiator corrosion).
3. Alloying with other metals (stainless steel is an alloy of iron and chromium—see chart of alloys, p. 314).
4. Covering the surface with paint.

Iron is sufficiently high in the activity series that it reacts with steam to produce hydrogen and magnetic iron oxide (Fe_3O_4), known also as ferrous-ferric oxide ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$).



This reaction occurs slowly in steam radiators and when the valve on a radiator is opened it permits the release of the accumulated hydrogen. A disastrous explosion may occur if an open flame is brought near one of these open valves.

Iron reacts with dilute acids to form hydrogen and ferrous salts.

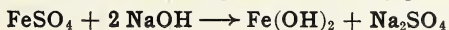


However, if concentrated nitric acid is used, the metal becomes **passive**, i.e. an adherent oxide film forms which prevents further action. This passivity is destroyed if the surface of the iron is scratched.

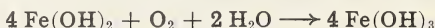
Compounds of iron. Iron is in Group VIII of the Periodic Table. Like the other elements in this group, it has variable valence and coloured compounds.

Iron forms two series of compounds—the ferrous (Fe^{++}) and the ferric (Fe^{+++}). **Ferrous compounds** are usually pale green in colour. Most of them are easily oxidized by atmospheric oxygen to ferric compounds. **Ferric compounds** are usually reddish-brown in colour.

Ferrous hydroxide [$\text{Fe}(\text{OH})_2$]. The mixing of a ferrous salt with a base produces a pale green precipitate of ferrous hydroxide which quickly changes through various shades of green to a muddy green colour.

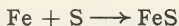


If the ferrous hydroxide is exposed to the oxygen of the air, it rapidly turns a reddish-brown colour due to the formation of ferric hydroxide.



Ferrous oxide (FeO), prepared by partial reduction of ferric oxide with hydrogen, is a black powder. It spontaneously returns to ferric oxide in air.

Ferrous sulphide (FeS) is formed by heating a mixture of iron and sulphur.

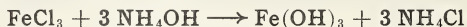


Pyrite (FeS_2) is a naturally-occurring sulphide of iron which because of its yellow colour is also called fool's gold.

Ferrous sulphate (FeSO_4) is probably the most important ferrous salt, and the green hydrate $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ is its commonest form. If equal molecular amounts of ferrous sulphate and ammonium sulphate are mixed in water and allowed to crystallize (by evaporating some of the water and cooling), a double salt, ferrous ammonium sulphate [$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$] is formed. Either this salt or ferrous sulphate can be used in the **brown-ring test** for the nitrate ion (p. 225). The formula of the dark brown compound formed in the brown-ring test is $\text{Fe(NO)} \cdot \text{SO}_4$ (ferrous nitrosyl sulphate—a complex compound of nitric oxide and ferrous sulphate). Ferrous sulphate is used as a *mordant* in dyeing and in making *ink*. A mixture of tannic acid (a complex organic acid obtained from nut-galls) and ferrous sulphate solution gives a colourless solution of ferrous tannate. Air oxidizes the ferrous tannate to insoluble black ferric tannate.

Ferric oxide (Fe_2O_3) is prepared by heating either ferric hydroxide or ferrous sulphate to a high temperature. The oxide prepared by the heating of ferrous sulphate is a red powder. It is used as a polishing powder (rouge) and as a pigment in cosmetics (venetian red). Ferric oxide is insoluble in water and is only moderately soluble in acids.

Ferric hydroxide [Fe(OH)_3] forms as a reddish-brown precipitate when a base is added to a solution of a ferric salt.



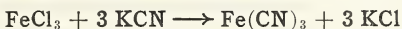
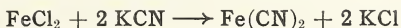
Ferric hydroxide is a very weak base and is not soluble in an excess of a strongly basic solution such as sodium hydroxide. This action is in contrast with the action of aluminum hydroxide with sodium hydroxide solution (p. 300).

Ferric chloride (FeCl_3) and **ferric sulphate** [$\text{Fe}_2(\text{SO}_4)_3$] are both soluble in water. They are moderately easily reduced to ferrous salts by such reducing agents as stannous chloride (SnCl_2), hydrogen with a platinum catalyst, zinc metal, and other active metals.

Ferric sulphate forms a double salt with ammonium sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24 \text{H}_2\text{O}$, exactly analogous to common alum. In fact, this salt is called ferric alum. More stable than the simple sulphate, ferric alum is often used for preparing solutions containing the ferric ion.

Cyanides of iron. Ferrous and ferric ions form a series of **complex cyanides** which have important uses both for identifying iron and for dyeing.

When potassium cyanide is added to solutions of ferrous and ferric salts, ferrous and ferric cyanides are produced.

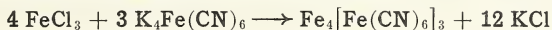


When excess potassium cyanide is added, the complex salts, yellow **potassium ferrocyanide** and red **potassium ferricyanide** are formed.



Both of these compounds are soluble in water.

The reactions of ferrous and ferric ions with potassium ferrocyanide and potassium ferricyanide give a series of four compounds of which two are important. For example, when a solution of a ferric salt is added to a solution of potassium ferrocyanide, deep blue **ferric ferrocyanide**, called **Prussian blue**, is precipitated.



Prussian blue is used as laundry blueing and as ink, and its formation is a test for the ferric ion.

Ferrous ferricyanide ($\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$), formed when a solution of a ferrous salt is added to potassium ferricyanide, is a dark blue precipitate very similar to Prussian blue and is called **Turnbull's blue**. Ferrous ferricyanide is used in blueprinting.

Potassium thiocyanate (KCNS) is also used to distinguish between ferrous and ferric compounds. Ferric salts give a red-coloured solution, whereas ferrous compounds give a nondescript brown colour.

Blueprinting. Blueprint paper is prepared by dipping paper in a mixture of potassium ferricyanide and either ferric oxalate or ferric citrate. The paper is then dried in air in the dark. When a drawing is placed over the dried paper and exposed to light, the light reduces the ferric ion of the ferric salt to the ferrous condition. Any lines on the original drawing block out the light and prevent this conversion from occurring. When the blueprint paper is placed in water, the reduced ion (Fe^{++}) reacts with the potassium ferricyanide to form

Turnbull's blue, which turns the paper blue, whereas the areas under the lines on the original drawing were not converted to the ferrous condition and hence the chemicals composed of original ferric compounds are washed away by the water, leaving the paper white. When the paper is dried, the dark lines of the original drawing appear as white lines on a blue background on the blueprint paper. Any excess potassium ferricyanide is washed out by the water.

EXERCISE

A

1. Name and give the formula for each of the three most important iron ores.
2. Make an outline map showing three important iron ore deposits in Canada.
3. What contributions did Smith, Low and Cross make to the development of the iron industry in Canada?
4. Why is the whole of North America so interested in Canada's new discoveries of iron ore?
5. Where is the Mesabi Range in relation to the Steep Rock deposit?
6. Draw a diagram of the blast furnace indicating the charge, lining, tuyeres, stack, hearth, hopper, cinder notch and tapping hole.
7. Explain the metallurgy of iron as carried out in the blast furnace. Illustrate your answer by equations.
8. Describe the Bessemer process including in your answer reference to the method of charging, the charge itself, impurities removed, the part played by the air-blast and the appearance of the reaction.
9. What are "spiegeleisen" and "ferromanganese"? What part do they play in the making of steel?
10. What are the chief uses of Bessemer steel? Why is this type of steel limited in its uses?
11. Why is the "open-hearth" process so named?
12. What is the fuel used in the open-hearth process and how is it preheated?
13. Of what is the lining of the open-hearth furnace composed?
14. What materials compose the usual charge of the open-hearth furnace?
15. Why does the charge placed in an open-hearth furnace vary in composition from time to time?
16. By the use of equations show how the impurities found in pig-iron are removed when it is processed in the open-hearth furnace.
17. What are the two types of electric furnace?
18. What is the main use of the electric furnace?
19. What part does temperature play in the shaping of finished steel?
20. What is tempering?
21. What properties are given to steel when it is cooled slowly? What is the result when it is cooled rapidly?
22. What is meant by case-hardening? State two ways in which case-hardening may be done.
23. Discuss the uses of steel in the modern world.
24. Why is rusting of iron an important chemical reaction?
25. What is passive iron?
26. Why does metallic iron displace copper from solutions of copper salts?

27. Ferrous hydroxide readily changes to ferric hydroxide in the presence of air. Explain.

28. Outline the procedure for the brown-ring test for a nitrate. Why is it necessary to use a freshly-prepared solution of the ferrous salt?

29. Why is it that a ferric hydroxide precipitate does not dissolve in excess sodium hydroxide solution, whereas a precipitate of aluminum hydroxide does dissolve in excess sodium hydroxide?

30. What are the uses of ferric oxide?

31. Devise a test (i) for ferrous ion, (ii) for ferric ion, using a potassium iron cyanide solution.

32. What are the two reasons for placing blueprint paper in water after exposure to light?

B

1. What would be some of the deficiencies of the iron produced by the ancients?

2. In the early part of the present century all pig-iron was cast into molds whether it was to be used in the manufacturing of steel or not. To-day most of it is poured into the "hot-metal" car. Name one advantage of the new method.

3. What is the purpose of the flux in the metallurgy of iron? Sometimes a basic flux (CaCO_3) is used and sometimes an acidic flux (SiO_2) is used. Explain.

4. When the Bessemer converter is tipped to a vertical position, why does the molten charge not flow down through the openings in the bottom of the converter?

5. Steel is plastic enough for rolling at 875°C . Why are the ingots raised to a temperature of 1300°C . before the rolling operation is started?

6. What advantages do alloy steels have over steel? Use information from the table of alloys to illustrate your answer.

CHAPTER 30

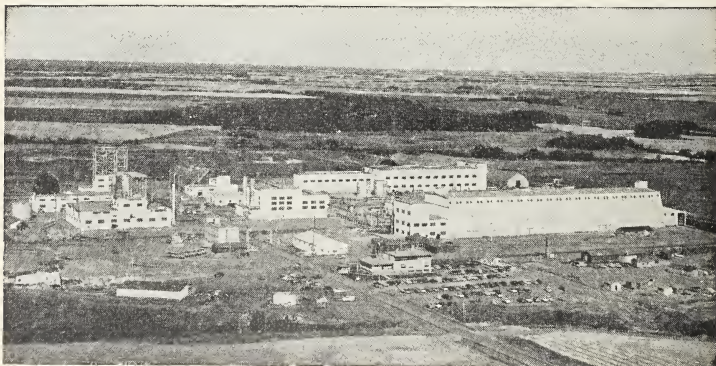
Copper

Who is able with powerful genius to frame a poem worthy of the grandeur of the things and these discoveries?

LUCRETIUS

Copper has been known for more than 6000 years and was one of the first metals to be used by man. It is believed that in the early ages it was mined in the free state, mixed with tin. In the first crude attempts to refine copper, it is likely that an alloy was produced rather than pure copper yet Egyptian statuettes made of pure copper have been found which date back to 2500 B.C. Archaeological discoveries indicate that in early times copper was used chiefly for ornaments, cooking utensils and weapons.

Canada as a producer of copper. Canada is producing more than 250,000 tons of copper a year from Canadian ores and approximately fifty per cent of this comes from the nickel-copper mines near Sudbury. Approximately twenty-six per cent is mined in Quebec, and sixteen per cent of the country's output is mined in Manitoba and Saskatchewan. Important operations are centred in the Flin Flon district as well as at Lynn Lake. Concentrates from these mines are taken to the new \$17,000,000 Sherritt Gordon refinery at Fort Saskatchewan, Alberta.



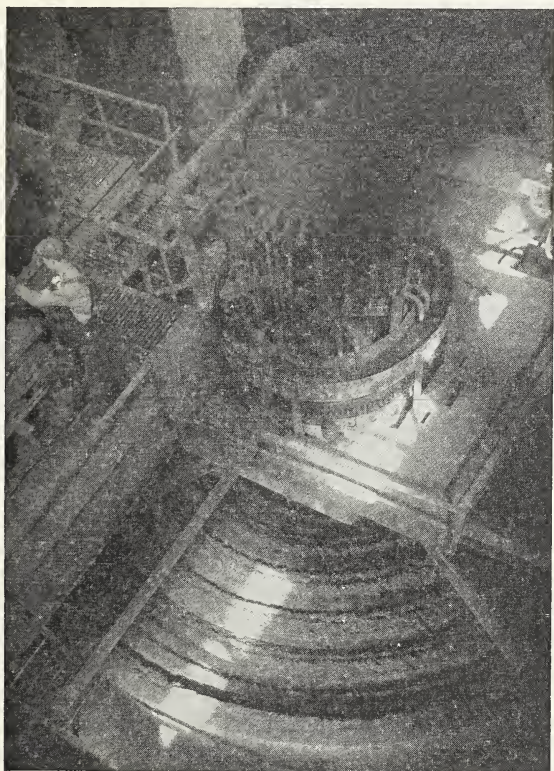
Alberta Gov't Photo by Chuck Ross

Fig. 30.1. Sherritt Gordon copper refinery.

At present eight per cent of Canada's copper comes from British Columbia, and recent surveys in the Portland Canal area have disclosed large deposits of copper hitherto untapped.

Although free (native) copper has been found in the Lake Superior region in Canada, the sulphide ores remain the most important sources from which we obtain the metal. The two most important copper ores are **chalcocite** (Cu_2S) and **chalcopyrite** (CuFeS_2). In some countries the oxide **cuprite** (Cu_2O) as well as the basic carbonates **malachite** [$\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$] and **azurite** [$\text{Cu}(\text{OH})_2 \cdot 2 \text{CuCO}_3$] serve as starting points for the metallurgy of copper.

Metallurgy of copper. The metallurgy of copper is a complex



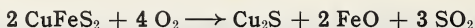
Anaconda Copper

Fig. 30.2. Roasting concentrate to partially remove sulphur.

process. The treatment given to Canadian ores, chiefly chalcopyrite, while it may differ slightly from one refinery to another, is in broad outline as presented here.

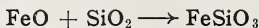
Concentration. Low grade ores ($\cdot 7\%$ to 5% copper) are concentrated by the froth-flotation process (p. 290) and then passed on to the roasters. It is not necessary to pass high grade ores through a flotation tank.

Roasting. The concentrate is placed in large furnaces where it is heated in the presence of air. Iron impurities unite with oxygen from the air and form ferrous oxide (FeO). The copper is converted into cuprous sulphide (Cu_2S). The resulting sulphur dioxide is vented to the atmosphere or collected and converted into sulphuric acid (p. 205).

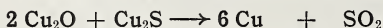
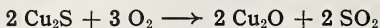


In addition to the cuprous sulphide and the ferrous oxide, the ore still contains all of the impurities—silica, gold, silver, selenium—that were originally present. The mixture of substances resulting from the roasting furnace is called **calcine**.

The reverberatory furnace. The calcine is transferred to a reverberatory furnace (Fig. 30.5) where a temperature of about 1650°C . is maintained by burning powdered coal. Here most of the FeO and SiO_2 react to form ferrous silicate (FeSiO_3) which is skimmed off, leaving Cu_2S and some FeS , with the metallic impurities, in the form known as **matte copper**.



The converter. The converter, sometimes described as a modified Bessemer, is lined with silica (SiO_2). When air is blasted through the converter, the remaining ferrous sulphide is oxidized to ferrous oxide which reacts with the silica lining to form slag. Part of the Cu_2S is converted into Cu_2O , and the remaining Cu_2S reacts with the Cu_2O to produce free copper and sulphur dioxide gas.



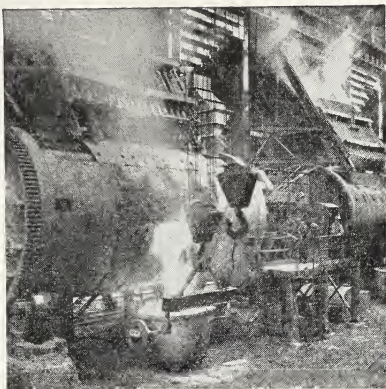
Any remaining ferrous oxide is removed by adding a weighed amount of SiO_2 which acts as a flux and forms a slag. The molten copper from the converter contains many bubbles of sulphur dioxide and is known as **blister copper**.

The anode furnace. The molten blister copper is put directly into an anode furnace where air is passed through to purify it further. This process oxidizes some of the copper and any residual iron or sulphur. The copper oxide is reduced again to metallic copper by introducing large poles of *green* wood into the molten metal. The

carbon in the wood unites with the chemically combined oxygen to form carbon dioxide and leaves the impure copper to be cast into 600 pound slabs which are used as anodes in the final process of refining. The product at this point is about 99 per cent pure. The remaining 1 per cent consists of gold, silver, zinc, nickel and platinum.

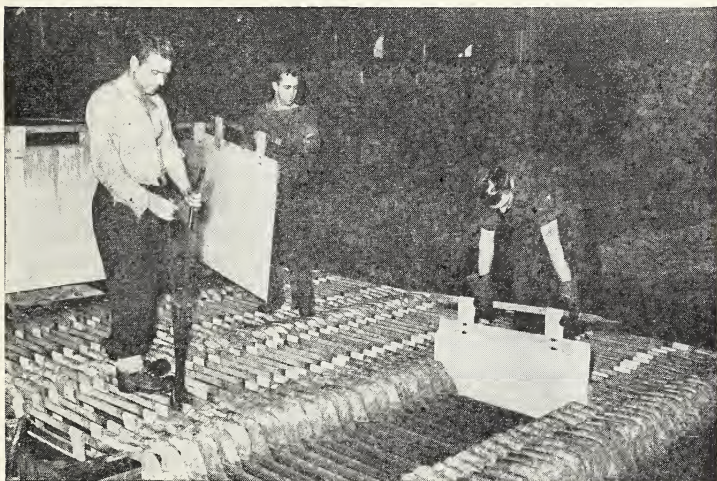
Electrolytic refining. The anode copper must be further purified because many of the uses to which copper is put demand a high degree of purity. This is especially important when the copper is to be used in wire for conducting electricity. The purifying process is completed in an electrolytic cell.

The anodes of the cell are the castings from the anode furnace.



Anaconda American Brass Limited

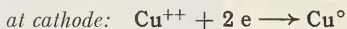
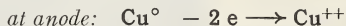
Fig. 30.3. Converter plant at Anaconda Reduction Works. Blister copper is being poured from the converter in the foreground.



International Nickel Company of Canada

Fig. 30.4. Inserting cathodes of pure copper.

The cathodes are thin sheets of pure copper. The electrolyte is a solution of copper sulphate. By careful voltage control the copper in the anode loses electrons to become cupric ions which are discharged at the cathode to produce pure copper.



The gold, silver, etc., are not brought into solution and fall to the bottom as **sludge (anode mud)**. The recovery of these impurities from the sludge helps to pay for the process.

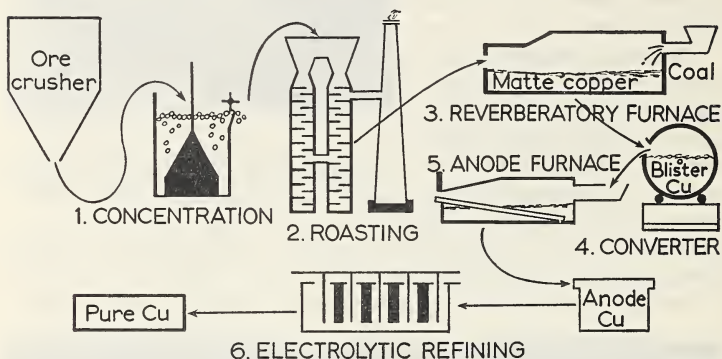


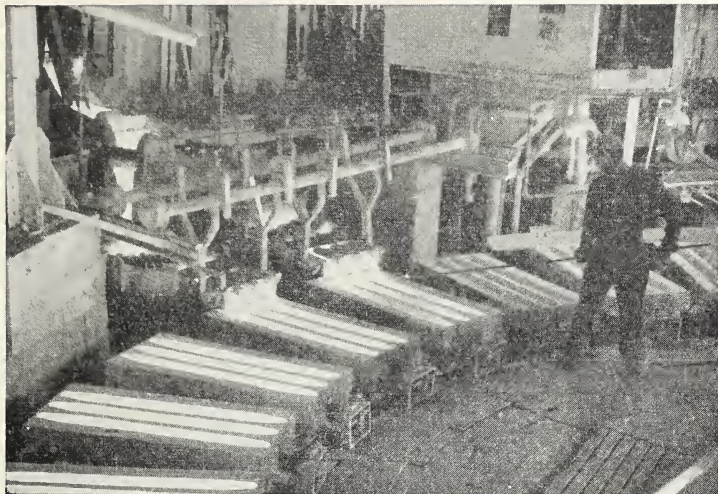
Fig. 30.5. Flow chart showing the making of copper.

Uses of copper. Copper is probably second only to iron in importance. The following represent only a few of the many uses of copper.

In the electrical field. At least 50 per cent of the copper produced to-day is used by the different electrical industries. These industries manufacture wire for the electric circuits in motors, for telegraph circuits, for telephone wires, for radio and television senders and receivers, for everyday appliances such as toasters, irons, etc.

In the construction and building trades. When exposed to moist air copper forms a basic copper carbonate $[\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3]$, sometimes called *patina*. This patina forms a protective coating, which makes copper useful for eave troughing, flashing, etc. Heating units and plumbing installations also use considerable amounts of copper.

In the processing industries. As copper is only slightly attacked by dilute acids (p. 326), it is used in containers and pipes where such



Anaconda Copper

Fig. 30.6. Casting copper bars for the making of wire.

chemical reactions are unimportant. Copper-bottomed kitchen utensils are popular because of the fact that copper is such an excellent conductor of heat.

In the printing trades. When a book like this text is to be printed, the words of each page are first set in type. After about 25,000 copies have been reproduced, the type is so worn that an electroplate must be made. A mold of the original type is taken in wax and dusted with graphite, which is a conductor of electricity. The graphite-covered mold is then used as the cathode in an electroplating tank, using a bar of pure copper as the anode in an electrolyte of copper sulphate solution.

Electro-deposition plates a thin shell of copper on the mold which, when the wax is melted away, is an exact copy of the original type but has a much harder surface. The shell is then filled with type metal and the resulting electrotype or electroplate will print up to 100,000 copies.

In the making of alloys. There are over 1000 alloys of copper which have been developed for specialized uses. Some of the more common alloys are given in the following table:

SOME ALLOYS OF COPPER

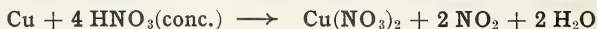
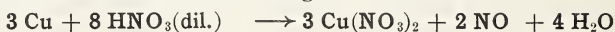
NAME	COMPOSITION	PROPERTIES	USES
Brass (300 varieties)	Cu, Zn	Withstands corrosion, easily worked	Hardware, instruments, stamped and drawn shapes, tubes, pipes
Bronze (many varieties)	Cu, Zn, Sn	High resistance to wear	Gears, bearings, bushings, hardware, stampings
Everdur	Cu, Si, Mn	High resistance to corrosion; can be welded	Water and sewer tanks, chemical and marine equipment
Nickel-silver (German silver)	Cu, Zn, Ni	Resists passage of electrical current	Elements in electric heater units, base metal for silver-plated ware
Coinage metal	Cu plus Ag or Ni	Cu hardens the alloy	Coinage, sterling silver

Physical properties. The most important property of copper is its ability to conduct electricity. It is a heavy metal with a density of 8.9 gm. per cc. It is malleable and ductile. Pure copper when heated can be drawn into a fine wire and it can also be shaped with ease. If copper is hammered, it becomes hard. Copper melts at 1083°C. and boils at 2300°C.

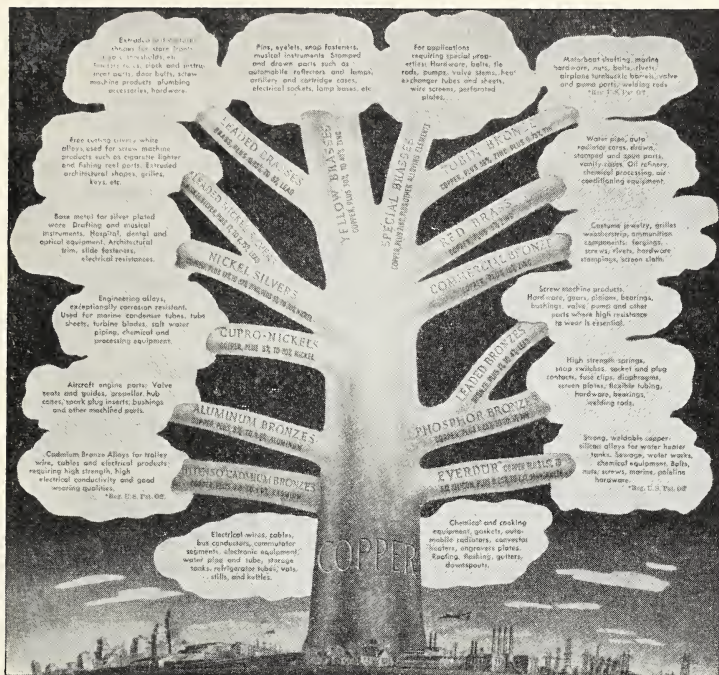
Chemical properties. Copper is below hydrogen in the activity series; in other words, it is a relatively inactive element. Because of its relative inactivity it is found in the elemental, or native state in nature.

Copper slowly tarnishes in moist air. Eventually a coating of the basic carbonate of copper is formed which gives the characteristic green colour to copper roofs in moist climates.

Copper will not react with acids to produce hydrogen and consequently appears below hydrogen in the activity series (p. 283). Copper is attacked, however, by oxidizing acids. For example, either cold, dilute or concentrated nitric acids will react with copper to produce water and oxides of nitrogen.



Copper forms two series of compounds, the **cuprous** (Cu^+) and the **cupric** (Cu^{++}) series. Although copper appears in Group I of the Periodic Table (p. 238) it has little in common with the alkali metals except its ability to form monovalent compounds.



Anaconda American Brass Ltd.

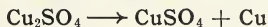
Fig. 30.7. The copper tree.

Usually cuprous compounds are white, instable solids only slightly soluble in water.

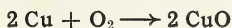
Cuprous compounds. All cuprous compounds are white except cuprous oxide (red) and cuprous sulphide (black). Cuprous oxide is precipitated from Fehling's solution in the test for glucose (Chapter 32).

Cuprous chloride (CuCl), similar to silver chloride, is insoluble in water.

Cuprous sulphate (Cu_2SO_4) is an unstable compound which decomposes in water to form copper and cupric sulphate.



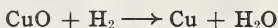
Cupric compounds. Cupric oxide (CuO) (black) is best prepared by burning copper wire or copper foil in air.



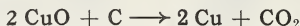
While it may be prepared by heating cupric nitrate, the product is not usually so pure as when prepared by burning copper in air.



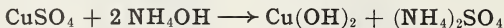
Cupric oxide can be reduced quite readily by hydrogen. The experimental apparatus for this reaction is given on page 51.



Cupric oxide is also readily reduced by carbon (e.g. poling of copper in an anode furnace).



Cupric hydroxide $[\text{Cu}(\text{OH})_2]$ may be precipitated as a light blue, gelatinous precipitate by slowly adding dilute ammonium hydroxide solution to a hot cupric sulphate solution.



Cupric hydroxide is a pale blue solid which is insoluble in both water and sodium hydroxide. If excess ammonium hydroxide is used, a soluble complex compound, cupric ammine hydroxide $[\text{Cu}(\text{NH}_3)_4(\text{OH})_2]$, with a deep blue colour is formed.

Cupric sulphate (CuSO_4) is the most important cupric salt. The anhydrous salt is white. The hydrated salt ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) is blue. Cupric sulphate is soluble in water and is used in copper electroplating cells and in electrolytic cells. It is very toxic to lower organisms, and small quantities are used in swimming pools and water reservoirs to kill algae. A mixture of slaked lime $[\text{Ca}(\text{OH})_2]$ and cupric sulphate is the fungicidal plant spray called **Bordeaux mixture**.

Paris green, which is used as a pigment and as an insecticide, is a double salt of cupric acetate and cupric arsenite $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}_3(\text{AsO}_3)_2]$.

Cupric ammine hydroxide, referred to above, dissolves cellulose from cotton or wood. When the resulting solution is extruded through fine nozzles into an acid bath, the acid neutralizes the ammonia, and the cellulose precipitates as long threads. This is the **Bemberg process** for making rayon.

EXERCISE

A

1. Discuss briefly the early uses of copper.
2. What is the most important property of copper?
3. Discuss Canada's role as a producer of copper.
4. Name and give the formulae of two Canadian minerals containing copper.
5. (a) Discuss the metallurgy of copper using the following topics: (i) concentration; (ii) roasting; (iii) production of matte copper; (iv) production of blister copper; (v) production of anode copper; (vi) electrolytic refining.
(b) Illustrate where possible with equations.

6. *Patina* is a protective coat. Discuss this as it applies to copper in the building trades.

7. The processing industries use much copper. Why is copper used in preference to zinc?

8. Describe the making of an electroplate.

9. Compare such alloys as brass, bronze and everdur under the headings composition, properties and uses.

10. What is the important property of nickel-silver?

11. Why is copper used in coinage metal?

12. Compare copper with iron and aluminum as to physical properties including melting point, boiling point and density.

13. Explain the action that takes place when copper reacts with (a) dilute nitric acid, (b) concentrated nitric acid.

14. In what way is copper similar to the alkali metals?

15. Except for cuprous oxide, the cuprous compounds are not very useful. Explain.

16. Why is cupric sulphate an important copper salt?

17. Give the composition and use of (a) Paris green, (b) Bordeaux mixture.

18. Briefly describe three ways of making rayon.

19. Cu^{++} and Fe^{++} are named respectively *cupric* ion and *ferrous* ion. Explain.

B

1. Copper is being replaced by aluminum in certain phases of the electrical industry. Discuss briefly.

2. The introduction of silicon gives alloys a definite property. Discuss this statement and illustrate by describing alloys of copper, aluminum and iron.

3. How would you test for the presence of copper in an alloy suspected of containing aluminum and copper?

4. Once a roll of copper pipe is straightened it is difficult to coil again. Explain.

CHAPTER 31

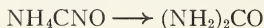
Organic Chemistry

Many compounds now referred to as organic must have existed on earth before life began, but only in very recent times has much progress been made in their study.

CARL NOLLER

One of the principal branches of chemistry is centred around a study of the compounds of the single element *carbon*. As the number of organic compounds is approximately twenty times greater than the total of inorganic compounds, the formation of a separate branch of chemistry is necessary.

Organic compounds. The name **organic chemistry** has been given to the study of the compounds of carbon because in the early days of chemistry most of the known carbon-containing compounds were associated with living matter. Up until 1828, scientists believed that the compounds produced by living processes could not be synthesized outside a living body. In that year Wöhler synthesized urea $[(\text{NH}_2)_2\text{CO}]$, a compound found in urine, by the interaction of two inorganic salts, ammonium sulphate and potassium cyanate. Ammonium cyanate (NH_4CNO), one of the products of this reaction, changes to urea by a simple shift in the structure of the molecule.



Organic chemistry was thus emancipated from 'vital-forces' and became a science in its own right. At present, the number of organic

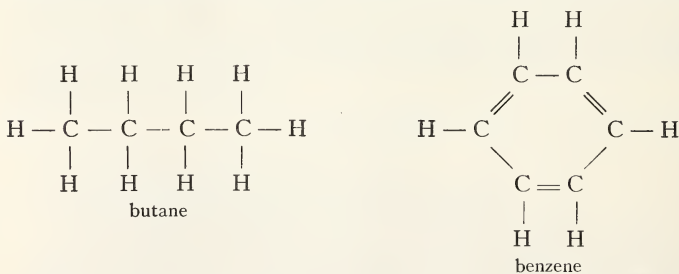
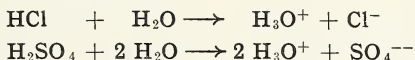


Fig. 31.1. Carbon atoms combine with other atoms and with themselves exhibiting a valence of four. Thus chains and rings of carbon atoms are formed, becoming the structural basis of most organic compounds.

compounds synthesized by chemists far exceeds the number found in living matter. The principal reasons that carbon is able to form so many compounds are (1) carbon has the relatively high valence of four and (2) carbon atoms join each other to form chains or rings (Fig. 31.1). The ability of carbon atoms to link together to form chains or rings is a characteristic of the lighter elements in Group IV of the Periodic Table (p. 238) and is most emphasized in carbon. When the carbon atoms combine with each other they do so by forming a covalent linkage.

Covalence. Covalence is the type of bonding or joining together of atoms which occurs in molecules of all acids and in gases such as H_2 , N_2 , O_2 , Cl_2 , and H_2O , CO_2 , NH_3 , SO_2 , NO , HCl , etc. When covalent compounds are dissolved in water they do not separate into ions; they may either go into solution in a physical sense or they may react with the water in a chemical sense producing hydronium ions, H_3O^+ (hydrated hydrogen ions).



This action with water is in contrast to the action with bases and salts which contain electrovalent bonds (p. 137) and which *do* dissociate into ions when dissolved in water.

The term molecule is customarily used only when referring to covalent compounds. Electrovalent compounds, held together as they are by electrostatic attraction, cannot claim this distinctive name. Many compounds contain both covalent and electrovalent bonds.

On page 131, valence bonds were represented by "arms" grasping each other between the adjoining atoms. In writing formulae, however, it is customary to use lines instead of "arms", and the symbols are linked together directly by the lines and are not enclosed in circles. For example, the structures of water and aluminum oxide are represented as shown in Fig. 31.2.

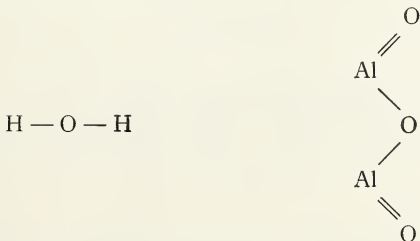


Fig. 31.2. The structural formula of water and of aluminum oxide.

The explanation of covalence. Chapter 13 indicates that in the case of **electrovalence**, the atoms transfer electrons by borrowing or lending them in order to acquire the stable octet structure as found in the nearest inert gas. In the case of **covalence**, the atoms **share** pairs of electrons (usually one from each atom) in order to acquire the same number as in the nearest inert gas. Thus, in hydrogen (H_2) each hydrogen atom shares its electron with the other so that a **shared pair of electrons** resides between the two atoms (Fig. 31.3). Each hydrogen atom now shares the same number of electrons as the stable helium atom. Similarly in chlorine (Cl_2) the outside ring of each chlorine atom shares one of its electrons with the outside ring of the other atom so that each atom holds (or shares in) the same number of electrons as found in the outside ring of the stable argon atom.

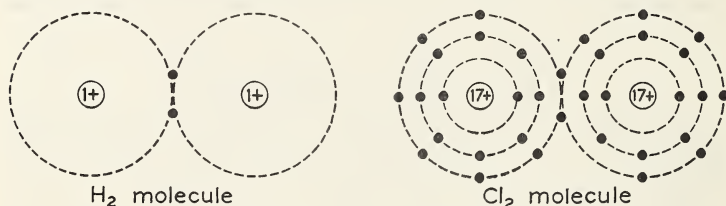


Fig. 31.3. The electronic structures of the hydrogen (H_2) and the chlorine (Cl_2) molecules. Each atom "shares" one electron with the other atom. The two "shared" electrons belong to both atoms of a pair. The two "shared" electrons constitute a single covalent bond.

The experimental difference between electrovalence and covalence is that the electrovalent bond comes apart in a water solution while the covalent bond does not.

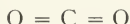
The same valence rules apply both to covalence and to electrovalence, and the calculation of the valence of each element in a simple compound is the same as given in Chapter 13. However, a difficulty arises when one tries to calculate the valences of elements in compounds in which the atoms of the same element are joined to each other. As this is the case for most organic compounds, other methods must be used. The use of **structural formulae** as shown in Fig. 31.1 overcomes the difficulty. **Single valence bonds** indicate one shared pair of electrons and are represented in a formula by a single line. **Double valence bonds** indicate two shared pairs of electrons and are represented by two lines.

Carbon atoms combine with each other and with other atoms by covalent bonds. Carbon in carbon compounds exhibits a valence of

four, and each carbon atom is represented as being surrounded by four

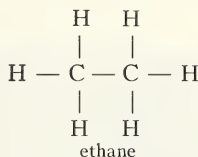
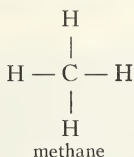
valence bonds, e.g. $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$ or $=\text{C}=\text{}$. One common exception to

the tetravalence of carbon is carbon monoxide (CO) an unsaturated molecule that readily takes on another oxygen atom to become carbon dioxide (CO₂) where carbon displays its usual valence of four.



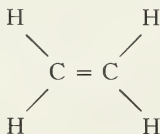
Structural formulae show (1) the relative positions of the atoms with respect to each other, as represented on a plane of paper or blackboard and (2) the number of valence bonds between the atoms.

Thus, the structural formulae of methane (CH₄) and of ethane (C₂H₆) are as follows:



Actually, the four valence bonds around each carbon atom in these compounds are distributed equally in three-dimensional space, and each valence bond that is not shared with a carbon is shared with a hydrogen. When valence bonds are shared in this way the compounds are said to be **saturated** with hydrogen.

Many compounds exist, however, where there are not sufficient hydrogen atoms to satisfy or saturate all of the carbon atoms. To explain the tetravalent nature of carbon in such cases, two carbon atoms are linked together, either by a **double bond** (C = C) where two pairs of electrons are shared, as shown in the formula for **ethylene** (C₂H₄)

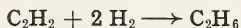


or by three pairs of shared electrons as represented by the **triple bond** in the formula for **acetylene** (C₂H₂)

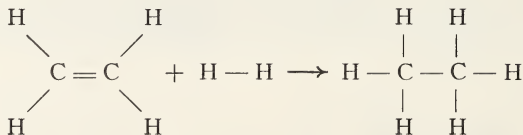


The double bond of **ethylene** and the triple bond of **acetylene** are said to be **unsaturated** bonds. Double bonds and triple bonds are places of weakness in the molecular structure and this weakness causes

these unsaturated compounds to be very reactive. In the series ethane—ethylene—acetylene, the reactivity of the compounds increases enormously. Ethylene and, even more so, acetylene have a great affinity for many substances including hydrogen. The addition of hydrogen to the unsaturated compounds may be shown by the following equations:

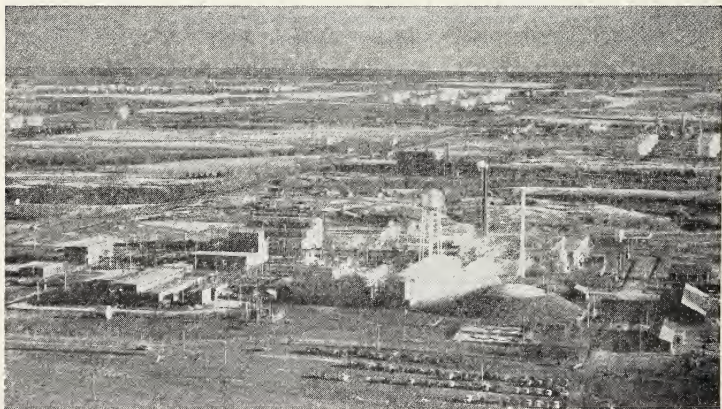


The addition of hydrogen to ethylene may be represented graphically as follows:



Experimentally, the addition of hydrogen to an unsaturated compound will take place only in the presence of a catalyst. Iron, nickel and platinum are metals which act as catalysts in these addition reactions.

Under certain conditions where the pressure is high and the temperature is above $100^\circ\text{C}.$, hundreds of ethylene molecules combine with



C.I.L.

Fig. 31.4. The Edmonton polythene (polyethylene) plant of Canadian Industries (1954) Limited. The plant produces the versatile polyethylene plastic from Alberta natural gas using some of the highest pressures known to man. In some instances pressures exceed 20,000 pounds per square inch.

themselves in long chains to form a substance called *polyethylene*. Polyethylene is a solid substance which is tough, flexible, and waxy to the touch. It melts at approximately 120°C . Polyethylene does not have an exact molecular weight as the number of molecules which pack together is variable. The number of carbon atoms in the chain may range from 100 to 1000.

The process in which a number of single molecules combine to form an enormous molecule is called **polymerization**. Rubber and plastics are **polymers**. The polymer polyethylene was discovered in Britain in the 1930's and is now produced in Canada at a plant near Edmonton, Alberta. In this plant, ethane from natural gas (see, for example, the composition of Leduc gas, p. 340) is converted to ethylene. The ethylene so produced is polymerized to polyethylene. Polyethylene has many industrial and home uses.

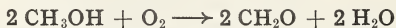


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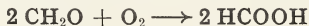
Fig. 31.5. A few of the wide variety of molded polyethylene forms.

Classification of organic compounds. Organic compounds can be divided into only a few types or classes, in spite of the relatively large numbers of these compounds. Each class has similar structures and

properties. The common classes into which organic compounds are divided are **hydrocarbons, alcohols and ethers, aldehydes and ketones, acids, and esters.** By substituting an OH group for a hydrogen atom in the hydrocarbon methane (CH_4), a hydroxyl derivative of methane known as methyl alcohol (CH_3OH) is formed. As oxygen has been added, methyl alcohol (CH_4O) is considered to be an oxidation product of methane (CH_4). Methyl alcohol may be oxidized to formaldehyde (CH_2O).

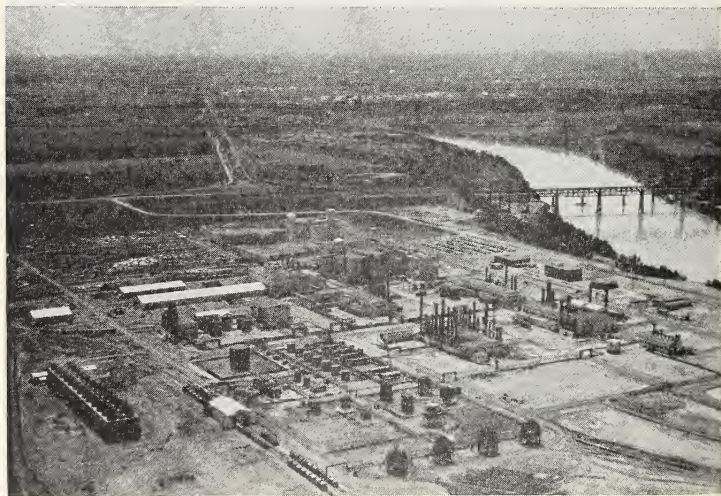


Formaldehyde may in turn be oxidized to formic acid (HCOOH).



The final oxidation product resulting from the combustion of any carbon compound is carbon dioxide (CO_2) in which carbon has a valence of four.

Beginning with any hydrocarbon represented by the general formula $\text{C}_n\text{H}_{2n+2}$, where n = number of carbon atoms, a corresponding alcohol, aldehyde and acid can be formed by successive oxidations. This is illustrated by the formulae in the table on the following page:



Richard Arless Associates

Fig. 31.6. General view of the Canadian Chemical Company plant, Edmonton, Alberta. The petrochemical department is in the right foreground. The cellulose acetate flake and yarn departments are in the middle background.

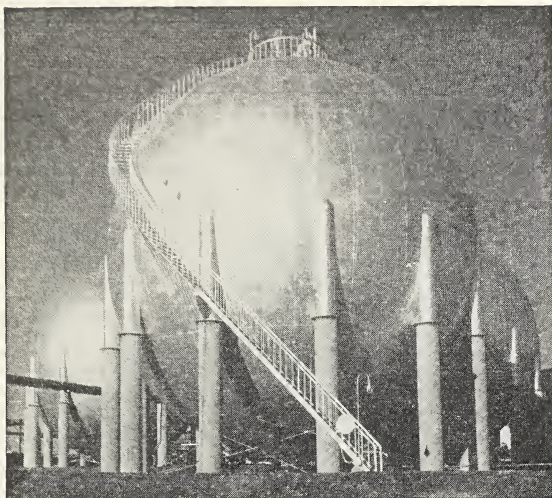
*Imperial Oil Limited*

Fig. 31.7. Butane storage spheres. Each of these spheres holds 15,000 barrels of butane which is obtained from the fractional distillation of crude oil. Butane is blended with gasoline to provide quick starting and is used in the manufacture of synthetic rubber.

HYDROCARBON	ALCOHOL	ALDEHYDE	ACID
CH_4	CH_3OH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC} \\ \backslash \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC} \\ \backslash \\ \text{OH} \end{array}$
C_2H_6	$\text{C}_2\text{H}_5\text{OH}$	CH_3CHO	CH_3COOH
C_3H_8	$\text{C}_3\text{H}_7\text{OH}$	$\text{C}_2\text{H}_5\text{CHO}$	$\text{C}_2\text{H}_5\text{COOH}$
$\text{C}_n\text{H}_{2n+2}$	$\text{C}_n\text{H}_{2n+2}\text{O}$	$\text{C}_n\text{H}_{2n}\text{O}$	$\text{C}_n\text{H}_{2n}\text{O}_2$

An excellent example of the industrial production of the above substances by the oxidation of hydrocarbons is provided by a petrochemical plant situated just outside of Edmonton, Alberta. In this plant the hydrocarbons, propane and butane, obtained from local natural gas, are oxidized with some air into a large variety of products (see simplified flow diagram, Fig. 31.8). These products are principally alcohols, aldehydes and ketones, and organic acids.

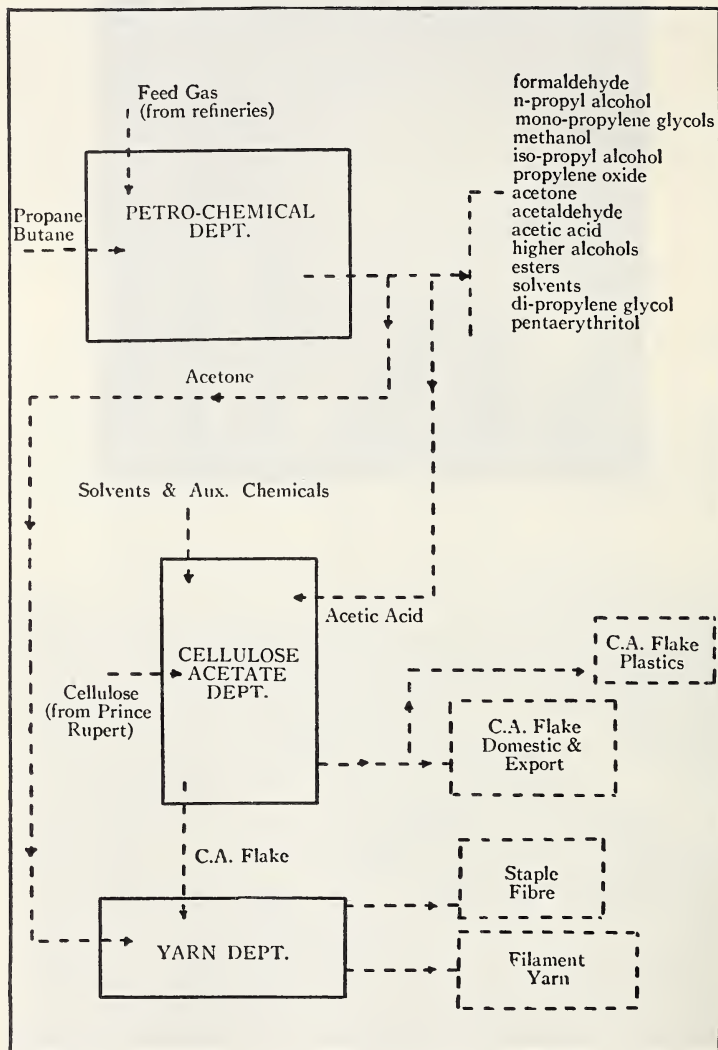


Fig. 31.8. Simplified flow diagram of the Canadian Chemical Company plant showing products obtained from the oxidation of hydrocarbons. (See also Fig. 31.6.)

Another method of classifying organic compounds depends upon the way in which the carbon atoms are held together. In some compounds the carbon atoms are linked together in long chain-like structures. Such chain compounds are known as **aliphatic hydrocarbons**. In other hydrocarbons the carbon atoms are linked together in such a way that they form ring structures. Such ring compounds are known as **aromatic hydrocarbons**.

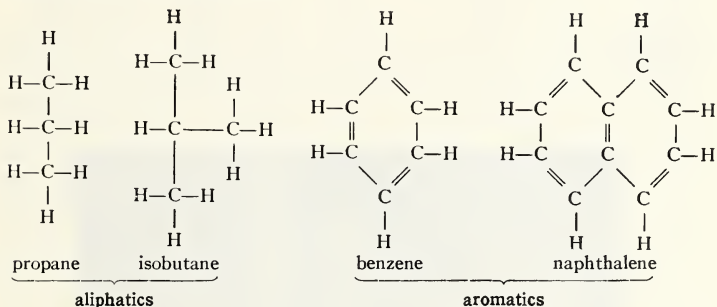


Fig. 31.9. Examples of some aliphatic and aromatic hydrocarbon compounds.

Hydrocarbons, alcohols, aldehydes and acids may either be chain structures or ring structures, and myriads of compounds are combinations of the two general structural forms. It is little wonder, therefore, that carbon compounds are so numerous.

Hydrocarbons. Compounds composed only of carbon and hydrogen are known as **hydrocarbons**. The simplest hydrocarbons form a series of **saturated** compounds known as the **paraffin** series (methane series), and the first and simplest member of the series is methane, CH_4 . The general formula of the series is $\text{C}_n\text{H}_{2n+2}$ in which n = number of carbon atoms. The first eight members of the methane series are

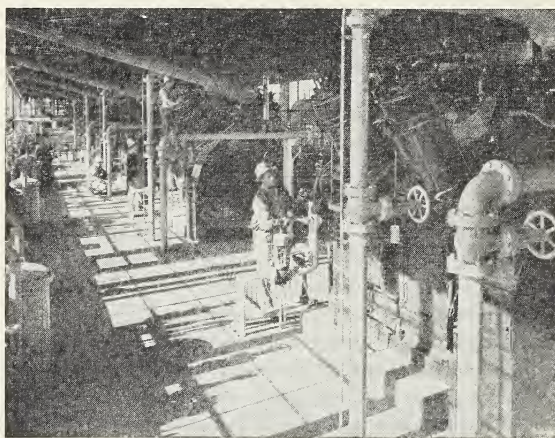
methane	CH_4	pentane	C_5H_{12}
ethane	C_2H_6	hexane	C_6H_{14}
propane	C_3H_8	heptane	C_7H_{16}
butane	C_4H_{10}	octane	C_8H_{18}

The paraffins constitute an **homologous series** where each succeeding member differs from the one before it by CH_2 . The lighter members, up to butane, are gases; the intermediate ones, from C_6 to C_{17} , are liquids; and those from C_{18} to as high as C_{100} are solids.

Natural gas is principally methane, with smaller amounts of ethane, propane and butane. In the following table are given the approximate percentage compositions of some of the natural gases of Alberta.

COMPOSITION OF NATURAL GAS IN SOME ALBERTA FIELDS

COMPOSITION	VIKING-KINSELLA	LEDUC	TURNER VALLEY	PINCHER CREEK
Methane	91.96	64.2	80.90	75.86
Ethane	1.89	19.7	9.05	3.30
Propane	0.72	10.8	3.42	1.18
Butane	0.25	3.5	1.58	0.75
Pentane	0.12	1.0	0.67	2.81
Nitrogen	5.06	0.0	—	—
Carbon dioxide	—	0.8	2.64	7.25
Hydrogen sulphide	—	—	1.74	8.85

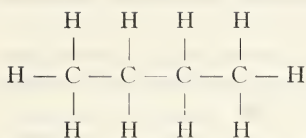


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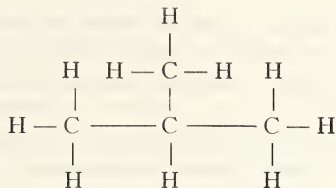
Fig. 31.10 A row of compressors at the polythene (polyethylene) plant of Canadian Industries (1954) Limited at Edmonton. In these compressors the components from natural gas are compressed at various stages in the first step—the making of ethylene.

Gasoline is a mixture containing hydrocarbons in the range from heptane to nonane (C_7 to C_9). **Fuel oils**, **lubricating oils**, and finally **paraffin wax** are mixtures of still larger paraffin molecules (see p. 187).

Isomerism. When valence rules are applied in writing the formulae of carbon compounds, it becomes evident that the same number of carbon and hydrogen atoms may have different arrangements of the atoms within the molecule, producing compounds having different properties.



normal butane (n-butane)



iso-butane

Both of these compounds have the same percentage composition but they differ considerably in their physical and chemical properties. For example, liquid n-butane boils at -0.6°C ., and iso-butane at -10°C .

Isomerism is the existence of two or more compounds with the same percentage composition and molecular weight but different properties. Isomers have different arrangements of their atoms within the molecules, as shown by their different structural formulae.

The number of isomers of the paraffin series of hydrocarbons alone is enormous. There is only one possible arrangement of atoms for each of methane, ethane and propane. Two isomers are possible for butane, three are possible for pentane; for octane, however, there are 19, and for eicosane ($\text{C}_{20}\text{H}_{42}$) there are over 100,000.

Anti-knock gasoline. An important application of isomerism is found in the oil refining industry. The production of gasolines with high "octane-ratings" (p. 188) requires special catalysts to convert straight chain hydrocarbons (e.g. n-hexane) into branch chain isomers (e.g. an iso-hexane). The straight chain compounds cause knocking in the internal combustion engine while their branch chain isomers do not.

Special tests are carried out at provincial government laboratories to find the "octane-ratings" of commercial gasolines. **Normal heptane** (C_7H_{16}), the straight chain isomer of heptane, has much higher knocking properties than straight-run gasoline from the refinery and is assigned an octane rating of zero. A highly branched isomer of octane (C_8H_{18}), called **iso-octane**, has much lower knocking properties than untreated gasoline. Iso-octane is assigned an octane rating of 100. To find the "octane-rating" of a particular gasoline, the performance of the gasoline in a standard engine is compared with the performance of various mixtures of n-heptane (0) and iso-octane (100). An "octane-rating" of 80 means that the gasoline performs the same as a mixture of 80 parts of iso-octane and 20 parts n-heptane. In Alberta, the "octane-ratings" of "regular" and "premium" gasolines are about 77 and 79 respectively.

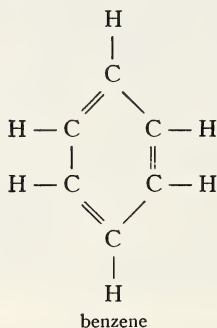
The "octane-rating" of gasoline is raised by isomerization, that is, by converting straight chain hydrocarbons into their branch chain

isomers. It is also raised by the addition of anti-knock compounds such as lead tetraethyl [$\text{Pb}(\text{C}_2\text{H}_5)_4$].

Highly branched hydrocarbons with "octane-ratings" greater than 100 have been produced, and these are used along with lead tetraethyl to make gasoline blends for aviation fuel.

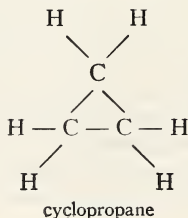
Other aliphatic hydrocarbons. The aliphatic hydrocarbons include a large variety of compounds, e.g. natural rubber and many synthetic rubbers, turpentine ($\text{C}_{10}\text{H}_{16}$), and carotene ($\text{C}_{40}\text{H}_{56}$, butter yellow) which is a source of vitamin A.

Aromatic hydrocarbons are carbon-hydrogen compounds that contain carbon atoms linked together in rings. Not all ring compounds are aromatics, but all aromatics contain one or more rings. The structural difference between aromatic ring compounds and other ring compounds is that aromatic compounds have alternate double and single bonds between the carbon atoms in the ring. For example, benzene (C_6H_6), which is the most important aromatic compound, has a structural formula as follows:



Benzene is a flammable liquid first obtained commercially by the distillation of coal (named benzol in Fig. 17.7, p. 170).

On the other hand, the ring compound cyclopropane (C_3H_6) is not an aromatic compound.



The anaesthetic properties of cyclopropane were discovered in 1929 by two Canadians, Lucas and Henderson, at the University of Toronto.

Naphthalene, $C_{10}H_8$, is an aromatic compound with a characteristic odour. It is used in moth balls.

Benzene derivatives are very important compounds. They are used in the manufacture of dyes, drugs, explosives, plastics, and many other substances.

Alcohols and ethers. The first step in the oxidation of a hydrocarbon produces an alcohol (p. 336). All alcohols contain one or more **hydroxyl groups** ($-OH$) but they are *not* bases (p. 158). In alcohols the ($-OH$) group is attached directly to a carbon atom. The names of alcohols end in *-ol*. For example, CH_3OH is **methyl alcohol**, or **methanol**.

Methyl alcohol (CH_3OH) is sometimes called wood alcohol because it can be obtained by the **destructive distillation** of wood. It is very poisonous, and if taken internally, may cause blindness and death. It is used in some anti-freezes and as an industrial solvent.

Ethyl alcohol (C_2H_5OH) is the most important alcohol. Most of it is obtained by the yeast **fermentation** of sugars. Although Pasteur (1822-1895) discovered that yeast was necessary to convert sugar to alcohol, Buchner later showed that the juice extracted from yeast cells which had been completely destroyed was capable of bringing about fermentation. The active substance in the juice is an **enzyme** called zymase (Chaper 32).

The chief sources of sugars for fermentation into alcohol are the various starches (corn, potato, rice) and sugar-cane molasses. Another important method of producing ethyl alcohol is by synthesis using ethylene, sulphuric acid and water.

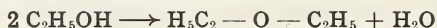
A sharp rise in the use of ethyl alcohol during World War II was due to its use in the synthesis of butadiene for the manufacture of synthetic rubber. In recent years, ethyl alcohol has been used for the manufacture of acetaldehyde and other chemicals, as an industrial solvent and as a radiator anti-freeze.

Alcohols with more than one hydroxyl group include **ethylene glycol** [$C_2H_4(OH)_2$ or $CH_2OH \cdot CH_2OH$], an important anti-freeze, and **glycerol** [$C_3H_5(OH)_3$] also popularly known as glycerine.

An important aromatic alcohol is **phenol** (C_6H_5OH), which is popularly called "carbolic acid". It is a very corrosive liquid which when used in proper dilutions is an effective disinfectant.

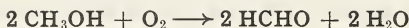
The **ethers** are related to the alcohols in the following way: Two molecules of ethyl alcohol, when treated with concentrated sulphuric

acid, part with one molecule of water to form a molecule of **diethyl ether**. Diethyl ether is used as an anaesthetic.



In general, the ethers contain the $-\text{O}-$ group.

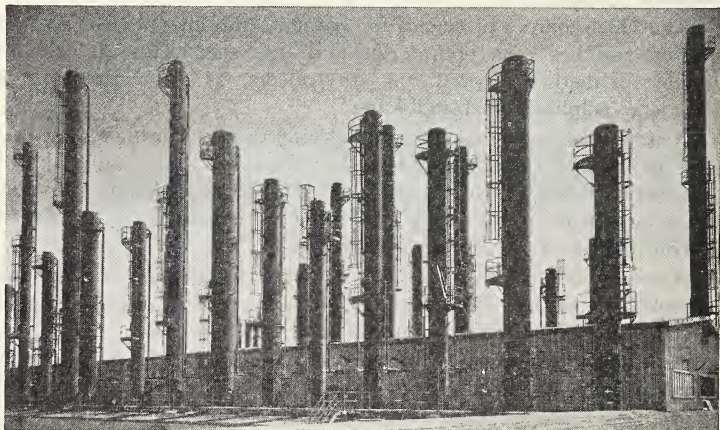
Aldehydes and ketones. The mild oxidation of alcohols produces **aldehydes** and **ketones**. **Formaldehyde**, the simplest aldehyde, is produced by passing methyl alcohol and air over a hot copper catalyst.



The structural formula of formaldehyde, $\text{H} - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{H}$ shows the

characteristic group, $-\overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{H}$, common to all aldehydes. Formaldehyde is familiar as a 40% solution by the name of **formalin**, which formerly was widely used as a disinfectant for grain smut. However, because improper usage may damage the grain, certain organic-mercury compounds are considered safer.

The **ketones** contain the group $-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-$ and the simplest one, **acetone** $[(\text{CH}_3)_2\text{CO}]$, is the most important. Acetone is very widely used as a solvent for cellulose nitrate in the manufacture of photo-

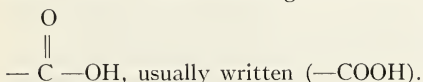


Richard Arless Associates

Fig. 31.11. Close-up view of the products purification unit, petrochemical department of the Canadian Chemical Company plant, Edmonton.

graphic film, lacquer "dopes" and explosives, and for cellulose acetate used in the manufacture of acetate rayon and photographic film.

Organic acids. Organic acids are usually prepared by the oxidation of either aldehydes or alcohols. **Formic acid** (HCOOH) and **acetic acid** (CH_3COOH) are the first two members of a series of acids known as the **fatty acids**. The name "fatty acid" originates from the fact that some of the higher members of the series, for example, **palmitic acid** ($\text{C}_{15}\text{H}_{31}\text{COOH}$) and **stearic acid** ($\text{C}_{17}\text{H}_{35}\text{COOH}$), are prepared from animal fats. All organic acids contain the **carboxyl** group,



Acetic acid is by far the most important industrial organic acid. Large amounts of it are used in the production of **cellulose acetate**. **Vinegar** contains about 5% acetic acid.

Other organic acids of a more complex nature are **lactic acid** ($\text{CH}_3\text{CHOHCOOH}$) in sour milk, **citric acid** [$\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3$] and **tartaric acid** (CHOHCOOH)₂ found in citrus fruits.

Soaps are usually mixtures of the sodium salts of palmitic and stearic acids. The calcium and magnesium salts of these acids are insoluble (see p. 264).

Esters. Esters are produced by a reaction between alcohols and acids. The ester, **ethyl acetate**, is formed from ethyl alcohol and acetic acid.



Esters usually have a sweet odour. The simpler esters are the substances that give the pleasant taste and odours to fruits. **Amyl acetate** has a pear-like odour, and **methyl butrate** smells like pineapple. Although the simpler esters are used for making artificial perfumes and flavours, their most important use is as solvents. The solvent used in quick-drying automobile lacquers is usually an ester.

Edible fats and oils are esters also and will be studied in the next chapter, which deals with the chemistry of foods.

Other organic compounds. **Carbon tetrachloride** (CCl_4) is used as a fire extinguisher, although it can be dangerous because it oxidizes to **phosgene** (COCl_2), a poisonous gas. Carbon tetrachloride is used as a non-flammable dry cleaning fluid, but its toxicity is a hazard.

Chloroform (CHCl_3) has been used as an anaesthetic and is an industrial solvent.

Freon (CCl_2F_2) is the most important fluorinated organic compound. It is entirely non-toxic, non-corrosive and non-flammable. It is widely used as a refrigerant in household refrigerators and air-

conditioning equipment. It is also used as a solvent-propellant for aerosol-type insecticides.

EXERCISE

1. Write the structural formulae of ammonia, sulphur dioxide, hydrogen sulphide, oxygen, hydrogen, phosphorus trioxide (P_2O_3), phosphorus trichloride (PCl_3) and silicon dioxide (SiO_2).
2. Write the structural formula of urea given the usual rules for the valences of carbon, hydrogen and oxygen and the fact that nitrogen has three covalent bonds in this compound.
3. By using the electronic structures of the constituent atoms, show the covalences of fluorine (F_2), methane and water.
4. In the series of compounds, acetylene—ethylene—ethane, the degree of saturation increases to a maximum. Why is ethane considered to be saturated, while the other two are unsaturated?
5. Show by their structural formulae the series of oxidation products resulting from the oxidation of normal butane (C_4H_{10}).
6. Write the balanced equation for the complete combustion of ethane.
7. If carbon dioxide is the compound in which carbon appears in its highest oxidation state and if most carbon compounds contain hydrogen, then in what compound will hydrogen appear in its highest oxidized form? Illustrate with turpentine ($C_{10}H_{16}$).
8. Explain why Leduc natural gas is an important source material for the petrochemical industry in Alberta.
9. Give the structural formulae of the three isomers of pentane (C_5H_{12}).
10. Show that the compounds urea and ammonium cyanate are isomers.
11. Give the structural formulae of ethyl alcohol and ethylene glycol.
12. Show by means of an equation that acetic acid reacts chemically as an acid.

CHAPTER 32

The Chemistry of Foods

But there is a part of life which can be grasped by chemical means, and there are chemically defined substances which can change the course of essential processes in living organisms.

EDUARD FARBER,

The **food** we eat is a **complex mixture** of organic compounds, inorganic salts and water. The food undergoes changes which in **biochemistry** are classified as **digestion**, **absorption** and **metabolism**. **Digestion** refers to the breakdown of food into simpler substances and occurs in the alimentary canal. **Absorption** is the transfer of the digested food into the blood stream. **Metabolism** refers to the chemical changes that occur in the body tissues after absorption of the food. The chemical changes occurring in these three processes are an important part of **biochemistry**, the science which links chemistry with biology.

In this chapter the chemical composition of foods and some of the chemical changes that these foods undergo during digestion will be considered.

Foods are divided into three broad groups: **carbohydrates**, **fats** and **proteins**. For the utilization of food, the body requires **vitamins**, **water**, and certain **inorganic salts** important for their mineral content and sometimes referred to as **minerals**.

Carbohydrates. Of the three groups of foods the **carbohydrates** are the simplest in chemical structure. The carbohydrates found in foods usually consist of sugars, starches and cellulose. **Sugars** such as glucose, fructose and sucrose are found in many fruits and vegetables. Sugar beets (Fig 32.1) and sugar cane are important sources of sucrose (table sugar). Honey is a mixture of glucose, fructose and sucrose. **Starches** are the stored form of carbohydrates in plants; for example, in potatoes, wheat and rice. **Cellulose** is the main component of the woody parts of trees and plants (see page 275).

The chemical structure of carbohydrates. Carbohydrates are composed of carbon, hydrogen and oxygen. The hydrogen and oxygen are usually in the same proportion as in water, that is, two atoms of hydrogen for each oxygen atom; for example, $C_6H_{10}O_5$, $C_6H_{12}O_6$, $C_{12}H_{22}O_{11}$. For this reason they are called carbohydrates



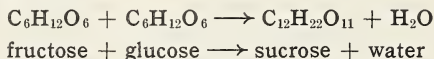
Alberta Gov't Photograph

Fig. 32.1. A beet sugar factory in Taber, Alberta.

(carbon hydrates). The name is misleading because hydrogen and oxygen do not exist as molecules of water in the carbohydrate molecule. Instead, there is a large number of hydroxyl (—OH) groups in the carbohydrates, and a few oxygen ($=\text{O}$) atoms as well. Thus carbohydrates are related to alcohols, aldehydes and ketones (Chap. 31).

Monosaccharides. Two important examples of carbohydrates are the sugars **glucose** and **fructose**. These are examples of **simple sugars**, or **monosaccharides**, and because each has the formula $\text{C}_6\text{H}_{12}\text{O}_6$ they are therefore isomers (p. 341). The monosaccharides form the basic units of the more complex carbohydrates.

Disaccharides. The disaccharides are compounds resulting from the combination of two monosaccharides with a loss of one molecule of water; for example:

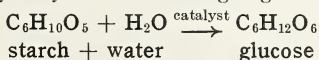


The two most common disaccharides are **sucrose** (a plant sugar) and **lactose** (an animal sugar). In the digestion of sucrose the above reaction is reversed producing simple sugars. Lactose (milk sugar) is a disaccharide containing glucose and galactose as its constituent monosaccharides.

Fehling's solution. A method of distinguishing between sucrose and the monosaccharides, fructose and glucose, is by means of Fehling's solution. Fehling's solution is a fresh mixture of a solution of cupric sulphate with a solution of sodium hydroxide and Rochelle salt

(sodium potassium tartrate). When Fehling's solution is added to glucose or fructose and heated, a red precipitate of cuprous oxide forms. Sucrose does not give this precipitate.

Polysaccharides represent a continuation of the union of simple sugar units into one giant molecule having properties quite different from the original simple sugars. Starch and cellulose are common examples of polysaccharides. The polysaccharides do not dissolve in water although some of them, starch for example, may be dispersed in it. **Starches** have from 300 to 1200 glucose units in their molecules. During digestion the fundamental starch unit is transformed by hydrolysis into the sugar glucose.

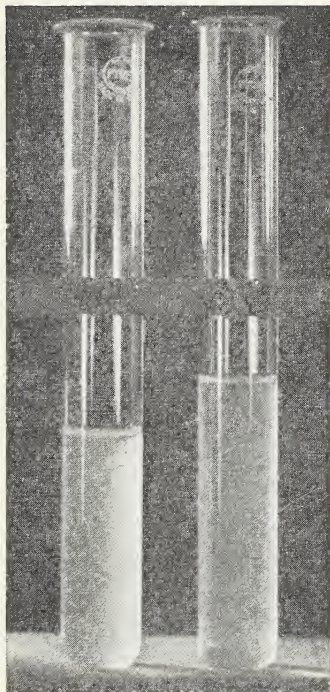


The breakdown of complex substances into simpler substances by the action of water is called hydrolysis. Water by itself will not hydrolyze starch very rapidly, and therefore a **catalyst** is necessary to increase the velocity of the reaction. In the digestion of foods, the catalysts are fluids secreted by salivary, gastric and intestinal glands and are known as **enzymes** (Fig. 32.2).

In the industrial production of corn syrup by the hydrolysis of corn starch, the catalyst is either dilute hydrochloric or sulphuric acid. In the digestion of starch, saliva is the enzyme that catalyzes the hydrolysis.

Starch-iodine test. The characteristic blue colour that starch gives with free iodine can be used to identify starch as well as iodine (see page 231 for the iodine test).

Cellulose is a complex polysaccharide containing from 600 to 3000 glucose units. It is a fibrous material because the glucose units are



J. L. Morrison

Fig. 32.2. The action of saliva on a starch suspension. The left-hand tube contains some of the original suspension. The right-hand tube contains the starch suspension to which saliva has been added and the mixture kept at 38°C. for one hour. The clearing of the suspension is due to the hydrolytic enzyme in the saliva.

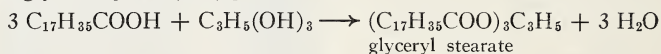
joined together in long chains. It is insoluble in water and cannot be digested by human beings or other mammals. However, northern caribou and reindeer have bacteria in their digestive tracts which hydrolyze cellulose into glucose.

Cellulose is a very important industrial raw material. It is the basic material in paper and in many fabrics such as cotton, rayon and celanese. **Rayon** and **celanese** are sometimes called artificial silks, but they are neither artificial nor are they silk. Natural silk is a protein. Most rayons are made by the viscose process (pp. 272-3). However, approximately 20% of the rayons are produced by the cellulose acetate process (celanese). In Alberta there is a large cellulose acetate plant just outside of Edmonton (Fig. 32.3). (See also Figs. 31.6 and 31.8 in previous chapter.)

Fats and oils. Another group of organic compounds which serve as foods and body components are the **fats** and **edible oils**. The difference between a fat and an oil is merely that a fat is a solid and an oil is a liquid at ordinary temperatures. Simple fats and oils contain carbon, hydrogen and oxygen, but some fats and oils are of a more complex nature and contain nitrogen and phosphorus. In this text the simpler fats and oils only will be considered.

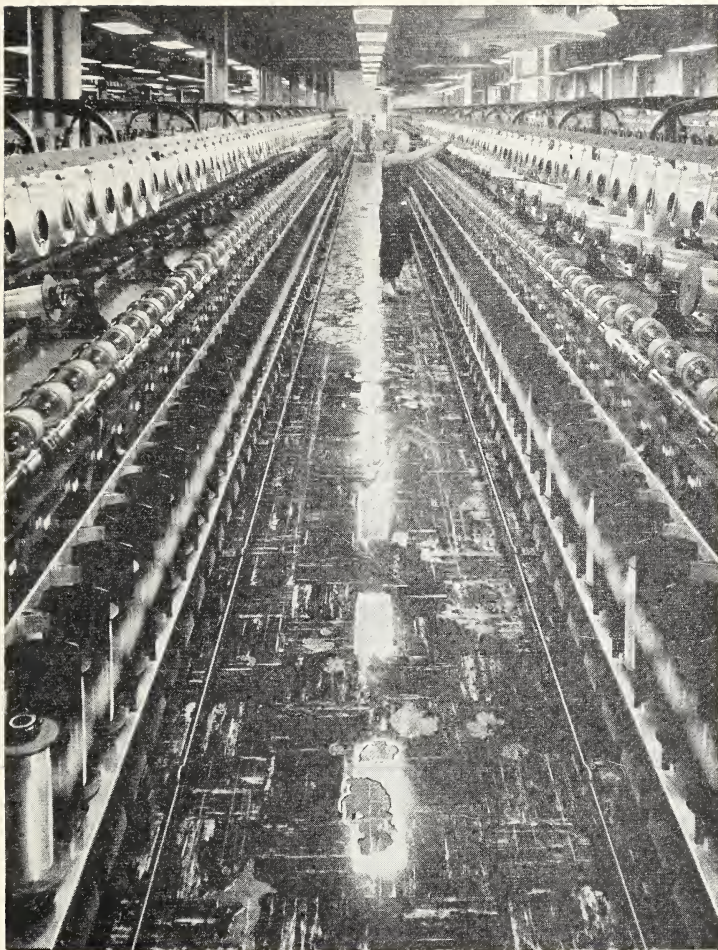
Fats and oils are insoluble in water, but soluble in ether, chloroform and acetone.

Fats and oils are esters (substances produced by the reaction of alcohols and acids) of higher fatty acids and glycerol. For example, **stearin** $(C_{17}H_{35}COO)_3C_3H_5$ is the ester of stearic acid $(C_{17}H_{35}COOH)$ and glycerol $[C_3H_5(OH)_3]$.



Natural fats and oils are complex mixtures of esters. Beef tallow contains esters of acids with 14, 16, and 18 carbon atoms. Vegetable oils also contain small amounts of an ester of a 20-carbon acid. Butter contains the same fats as contained in beef tallow and in addition esters of butyric (C_4) and caproic (C_6) acids. When butter goes rancid, the characteristic odour produced is due to the released butyric and caproic acids.

Vegetable oils. These oils contain a much larger proportion of unsaturated acid esters than do animal fats. That is, one or two double bonds occur between some of the carbon atoms in the carbon chain of the acid. The addition of hydrogen to these double bonds converts them to saturated acid esters. The saturation of the double bond raises the melting point of the oil until it becomes a fat. This saturation by hydrogen, called **hydrogenation**, is accomplished with



Richard Arless Associates

Fig. 32.3. View of the twisting machines in the yarn department of the Canadian Chemical Company plant (Edmonton). The plant produces cellulose acetate yarn, also called celanese.

nickel as a catalyst. The conversion of vegetable oils to fats is usually carried out at meat packing plants. The solid fats package more easily at the factory and are easier for the housewife to handle.

The butter substitute, **margarine**, ordinarily consists of about 80% fat, 17% milk and 3% salt and is obtained by the hydrogenation of vegetable oils such as coconut oil and cottonseed oil.

Linseed oil, the oil pressed from flaxseed, is used as a "drying" oil in paints.

Digestion of fats and oils. The end products of the digestion of fats are fatty acids and glycerol. Digestion of fats occurs in the stomach and intestine. The fats are hydrolyzed in the presence of the enzymes, **lipase** and **steapsin**.



These products, on entering the blood, are again converted to fats to become a part of the process of metabolism.

Proteins. Proteins are the most complex of the components of food. Proteins are present in all living tissue. Certain tissues, such as seeds and flesh, contain a higher proportion of proteins than do fatty and structural tissues. The nitrogen cycle in Chapter 24 illustrates the importance of proteins.

Proteins not only feed man but also help to clothe him. Meat, cheese, and eggs contain proteins. Shoes and wool fabrics are proteins. Natural silk is a protein excreted by the silkworm when it builds a cocoon for the pupa stage in its metamorphosis.

Four elements are present in all natural proteins: carbon, hydrogen, oxygen, and nitrogen. In addition to these elements many proteins contain sulphur with smaller amounts of other elements such as phosphorus, iron, and iodine, which are essential constituents of certain proteins. The haemoglobin of blood contains iron. Most proteins contain about 53% carbon, 7% hydrogen, 23% oxygen and 16% nitrogen. The nitrogen content of proteins distinguishes them from carbohydrates and fats.

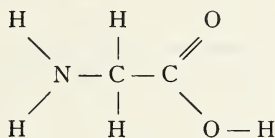
Protein molecules are large in size and complicated in structure. The molecular weights of proteins range from 10,000 to several million. All proteins are built from over 25 different building blocks called **amino acids**. At present, chemists believe that many of the amino acids are joined in chains within the protein molecule.

By applying the permutations and combinations of mathematics to the 25 different amino acid building blocks, the great number of different proteins that could exist may be envisioned. The work of unravelling the structures of many of the proteins is just beginning, and a great new field of research is now open to physical and organic chemists. Since proteins make up the essential component of living

matter their study is of special interest and importance. Moreover the **viruses**, which are living matter and which cause disease in both plants and animals, are believed to be very complex protein molecules, and chemists now speak of "the molecular weight of a virus". The *bushy stunt* virus has a "molecular weight" of about 10,000,000.

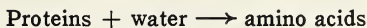
The complete hydrolysis of a protein produces its constituent amino acids.

The simplest amino acid is **glycine**, which has the following structural formula:



Glycine has a structure very similar to acetic acid with the difference that one of the hydrogen atoms on the first carbon next to the carboxyl group is replaced by an amino (NH_2) group. Thus, glycine is also called **amino acetic acid**. All amino acids have an amino group attached to the carbon next to the carboxyl group.

Digestion of proteins. In the digestion of proteins, enzymes in the gastric and intestinal juices catalyze the hydrolysis of the proteins to amino acids.



The amino acids pass into the blood stream. Thus, along with the hydrolyzed products of carbohydrates and fats, the amino acids enter into metabolism.

The xanthoproteic test for proteins consists of the reaction of a protein with concentrated nitric acid (p. 253). The protein turns to a yellow-coloured substance, which is believed to be an addition of nitric acid to parts of the protein molecule. If concentrated nitric acid is accidentally dropped on skin or fingernails, the yellow xanthoprotein compound appears.

Proteins are extremely sensitive to heat and certain other forms of energy. Above 65°C . many proteins undergo permanent changes called **denaturation**. An example of this permanent change takes place in the cooking of an egg. The egg white coagulates and can never be returned to its original condition. In denaturation the very complex arrangement of the protein molecules is partly or wholly destroyed. Another example of denaturation is the dangerous effect

of ultraviolet light on the eyes. This light coagulates the protein in the eyes and causes permanent damage. For this reason, welders wear special goggles.

Vitamins. Vitamins are accessory dietary compounds essential in maintaining at a normal level the metabolic processes in animals.

Until early in the 20th century an adequate diet was believed to consist of sufficient carbohydrates, fats, proteins and inorganic salts. Since that time vitamins have been discovered and at present over 15 are known. Their absence from the diet leads to various deficiency diseases, but the amounts of vitamins required in an adequate diet are very small compared with the amounts of ordinary foods. For example, the recommended daily requirement of vitamin C is 0.075 gram whereas that of protein is 70 grams.

The following are the sources and the significance of the more important vitamins.

Vitamin A is essential for growth and normal vision. An early deficiency symptom is night blindness. Recent research has shown that night blindness is fairly common. The chief natural sources of vitamin A are leafy green plants, fish-liver oils, eggs, butter, and cream.

Vitamin B₁ (thiamin) is essential for the maintenance of good appetite and digestion. Deficiency of B₁ leads to retarded growth, loss of appetite, emotional instability, and a disease called beriberi. The chief sources of this vitamin are liver, yeast, milk, eggs, fruits, and legumes.

Vitamin B₂ (riboflavin) is necessary for the growth and respiration of all tissues and cells. Deficiency symptoms are cracked and sore lips and dimness of vision. It is closely related to B₁ and is found in many of the same foods.

Niacin (nicotinic acid) is part of the **vitamin B complex** and is required for normal growth. The lack of niacin produces pellagra, a disease with extensive pigmentation on exposed parts of the skin. Sore and swollen tongue and loss of appetite also accompany pellagra. Niacin is found in the same foods as B₁ and B₂.

Vitamin C (ascorbic acid) is necessary for the formation and maintenance of tooth and bone tissue. The best known deficiency disease is scurvy. Dental caries and slow healing of wounds are also deficiency symptoms. Vitamin C occurs in citrus fruits, cabbage, raw turnips, and tomatoes.

Vitamin D regulates the calcification of bone structure. The lack of vitamin D leads to rickets (bowed legs, pigeon chest) and tooth decay. The important sources are fish-liver oils, mackerel, herring, sardines, egg yolk, and liver.

Vitamin K promotes the normal clotting of blood. Vitamin K deficiency leads to poor healing of cuts and other wounds. It is found in spinach, cabbage, cauliflower, carrot tops, and tomatoes.

CANADA'S FOOD RULES

Approved by the Canadian Council on Nutrition, May 1949)

These foods are good to eat. Eat them every day for health.
Have at least three meals each day.

1. **MILK:**
Children (up to about 12 years): at least 1 pint.
Adolescents: at least $1\frac{1}{2}$ pints.
Adults: at least $\frac{1}{2}$ pint.
2. **FRUIT:**
One serving of citrus fruit or tomatoes or their juices; and one serving of other fruit.
3. **VEGETABLES:**
At least one serving of potatoes; and at least two servings of other vegetables, preferably leafy, green or yellow and frequently raw.
4. **CEREALS AND BREAD:**
One serving of whole grain cereal, and at least four slices of bread (with butter or fortified margarine).
5. **MEAT AND FISH:**
One serving of meat, fish, poultry or meat alternate such as dried beans, eggs or cheese. Use LIVER frequently.

In addition:

Eggs and Cheese at least three times a week each.

VITAMIN D:

At least 400 International Units Daily for all growing persons and expectant and nursing mothers.

IODIZED SALT is recommended.

An adequate daily diet for a moderately active adult is about the same as that for a young adolescent (13-15 years). This diet consists of about 3 ounces of protein, sufficient carbohydrates and fats to give a total energy content of 3000 calories, 0.7 gram of calcium, 1.3 grams of phosphorus and 0.015 gram of iron.

A properly balanced diet will contain sufficient vitamins so that they need not be taken as a supplement. (See Canada's Food Rules above.)

In the following table showing the composition of some common foods, the minerals include calcium, phosphorus and iron. Vitamins are listed in those cases where the food is a good source. Otherwise, where the source is only fair, a superscript "f" follows the vitamin.

THE COMPOSITION OF COMMON FOODS

(Except for the vitamins, all the data is taken from the Table of Food Values Recommended for Use in Canada, by the Nutrition Division, Dept. of National Health and Welfare, Ottawa, Canada.)

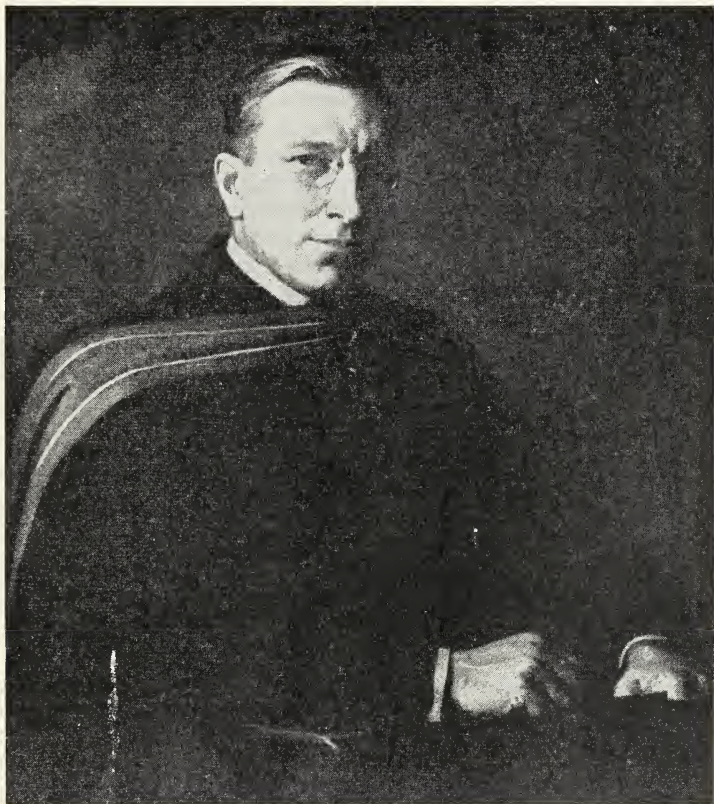
FOOD	CAL- ORIES PER LB.	WATER %	PRO- TEIN %	FAT %	CARBO- HYDRATE %	MIN- ERALS %	VITAMINS (N = niacin)
Apples	232	84.1	0.3	0.4	14.9	0.02	A ^f B ₁ B ₂ ^f C N
Bacon, back	1047	56.0	22.1	15.0	0.3	0.21	A ^f B ₁ B ₂ ^f
Beans, green	162	80.0	2.2	0.2	6.9	0.14	A B ₁ ^f B ₂ ^f C
Beef, round	746	59.0	17.6	10.0	0.0	0.17	A ^f B ₁ ^f B ₂ N
Bologna	1004	62.4	14.8	15.9	3.6	0.12	A ^f B ₁ ^f B ₂ ^f
Bread, white	1247	34.7	8.5	3.2	51.8	0.17	A ^f B ₁ ^f
Bread, whole wheat	1089	36.6	9.3	2.6	49.0	0.31	A B ₁ B ₂ ^f
Butter	3248	15.5	0.6	81.0	0.4	0.04	A D
Cabbage	90	67.5	1.0	0.1	3.9	0.06	A ^f B ₁ ^f B ₂ ^f C K
Carrots	173	77.6	1.1	0.3	8.2	0.07	A B ₁ B ₂ ^f C
Cheese, cheddar	1804	37.0	25.0	32.2	2.1	1.22	A B ₂
Eggs	737	74.0	12.8	11.5	0.7	0.27	A B ₁ B ₂ ^f D
Halibut	515	61.1	19.0	3.6	0.0	0.22	A ^f B ₁ ^f
Lettuce	77	94.8	1.2	0.2	2.9	0.05	A B ₁ B ₂ C D ^f
Liver (beef)	618	69.7	19.7	3.2	6.0	0.37	A B ₁ ^f B ₂ C N
Milk	294	87.0	3.5	3.5	4.9	0.22	A B ₁ ^f B ₂ D ^f
Oatmeal	1794	8.3	14.2	7.4	68.2	0.46	B ₁
Orange juice	199	87.5	0.8	0.2	11.0	0.04	A B ₁ ^f B ₂ ^f C
Peaches	183	76.5	0.4	0.1	10.6	0.03	A B ₁ B ₂ ^f C
Peanuts	2537	2.6	26.9	44.2	23.6	0.47	B ₁ N
Peas	430	74.3	6.7	0.4	17.7	0.15	A ^f B ₁ B ₂ C ^f
Potatoes	318	65.4	1.7	0.1	16.0	0.06	A B ₁ ^f C ^f
Rice, white	1629	12.3	7.6	0.3	79.4	0.16	
Salmon (canned)	784	67.2	20.2	9.6	0.0	0.61	A B ₁ ^f D N ^f
Spinach	102	92.7	2.3	0.3	3.2	0.14	A B ₁ B ₂ ^f C D K
Tomatoes	96	92.2	1.0	0.3	3.9	0.04	A B ₁ D ₂ ^f C K
Turnips	181	89.1	1.1	0.1	8.9	0.10	A ^f B ₁ ^f B ₂ ^f C

Hormones. Hormones are complex organic compounds which are the secretions of the **endocrine** or **ductless glands**. **Insulin**, for example, is a protein, and **thyroxin** is a complex iodinated amino acid. Hormones are released into body fluids such as the blood stream, and have specific effects on various organs and glands.

Adrenalin, for example, the first hormone to be synthesized, is excreted by the adrenal glands which are situated above the kidneys. Adrenalin increases the blood pressure, accelerates the heart beat and

counteracts the effect of excessive insulin. Hormones are sometimes called chemical messengers because they regulate and control the various processes (growth, metabolic, reproductive) occurring in the body.

The hormone **insulin** is of particular interest to Canadians. In 1922, Banting, Best, and Macleod, working at the University of Toronto, discovered insulin and for this discovery were awarded Canada's only Nobel prize. Insulin is excreted by the pancreas and regulates carbohydrate metabolism. If insulin is not produced in sufficient amounts by the pancreas, a disease known as diabetes mellitus develops.



University of Toronto

Fig. 32.4. Sir Frederick Banting.

Many disease conditions occur when the hormone secretions become unbalanced. Chemists, by discovering the chemical structures of most of the hormones, have increased both our knowledge and our control of many living processes.

Chemotherapy. In 1909, Paul Ehrlich synthesized the organic compound called **salvarsan** which was found to kill the organism causing syphilis. Thus, Ehrlich, by synthesizing chemical compounds that are more toxic for disease organisms than for the host, opened up a new field of chemistry. He gave this field of science the name chemotherapy.

In the 1930's, **sulphanilamide** and the other sulpha drugs were found to be effective against streptococcal infections. The production of sulpha drugs reached a high point in 1945. After that time, the importance of these drugs was reduced by the discovery of **penicillin** and a whole host of other **antibiotics**, although sulpha drugs are still important for treating certain diseases.

The antibiotics are very complex organic compounds produced by various molds. Some kill specific disease organisms; others kill a wide variety of them. New antibiotics are being discovered every year. Names such as **aureomycin**, **streptomycin** and **chloromycin** are already well known.

The effects of the indiscriminate use of the various antibiotics and other chemotherapeutic agents are not completely known, and these drugs should be used only under the direction of a competent medical doctor.

EXERCISE

1. Fats are an important part of the human diet. What other uses are made of fats?
2. What is a carbohydrate? Which carbohydrates are digestible by man? What other uses are there for carbohydrates?
3. An old home-method of making soap was to add lye (sodium hydroxide) to kitchen fat. Using glycerol tristearate as the fat, show by equations that soap (p. 267) and glycerol are produced.
4. What is a protein? Are all proteins useful as food? What proteins are dangerous to man?
5. The melting point of oleic acid ($C_{17}H_{33}COOH$) is $14^{\circ}C$. The melting point of stearic acid is $69.4^{\circ}C$. The oleic acid molecule contains one double bond, and for this reason it has two fewer hydrogen atoms than the stearic acid molecule. How do these facts explain the *hardening* of oils to fats by means of hydrogenation?
6. The same fundamental chemical process occurs in the digestion of carbohydrates, fats and proteins. Name the process and by means of a word equation illustrate it for each of the classes of foods.

7. What part is played by the enzymes in the process dealt with in question 6?

8. The energy yield of fats is about twice that of an equal weight of carbohydrates. Examine the table on food composition for evidence of this statement.

9. The principal minerals included in the table on food composition are calcium, phosphorus, and iron compounds. Why are these important in the diet?

10. Both vitamins and hormones are complex organic compounds. In what general way do they differ from each other?

CHAPTER 33

Chemistry and the Future

Necessity is the mother of invention.

FARQUHAR

Without chemical research and the scientific application of its results, Great Britain and her allies could not have won World War II, although to a large extent Mr. Everyman was kept in ignorance of many important discoveries that made victory certain. Once the censorship was lifted, a marvellous new era unfolded to give a glimpse of future wonders. For centuries, man worked with stone, cunningly fashioning crude implements of agriculture and warfare. With increased knowledge, the Age of Stone was succeeded by the Bronze Age and this, in more recent times, was followed by the Age of Steel. We are now standing on the threshold of a new era which could truly be called the Age of Chemistry.

During a national emergency brought about by war, the attention of chemists is focussed on the production of materials necessary to prosecute the war. In World War II, the allied nations' loss of many vital sources of raw rubber necessitated the discovery and production of synthetic substitutes. Employment of faster aeroplanes and jet propulsion caused a demand for different and better fuels. Many new alloys were needed for use in the lighter, well protected planes and in the amazing devices connected with location finding and signalling. The tropical warfare of the Pacific theatre of combat made imperative the discovery of new drugs and vaccines with which to fight disease, a much more powerful enemy than bullets or bombs. Then there was the ever-present need to produce food for our armies and the people of the liberated countries. A knowledge of chemistry was also necessary in the production of new fertilizers, and in finding new sources of vitamins.

The triumph of the scientific method has brought about the greatest material advance in human history. Knowledge gained by controlled experiments and objective reasoning from observed facts has led to great achievements. Although there apparently is no limit to creative chemistry, the scientist continues to appreciate the significance of

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theory in explaining his laboratory observations, e.g. the formulation of the atomic theory had much to do with the development of the atomic bomb and the release of atomic energy.

Practically every industry depends on the same basic raw materials: coal, limestone, salt, wood, sulphur, air and water. We have reason to believe that the great industries of the future will make use of raw materials from many additional sources.

In 1915, magnesium was five dollars a pound. Today, when manufactured from sea-water, it costs but twenty-two cents per pound. Because sea-water contains traces of practically every known element, it enters into the manufacture of many materials besides magnesium, e.g. bromine and bromine compounds. Will "The Salt Water Industry" become more important than the coal tar and petroleum industries? Creative chemists have carefully studied another raw material, the soya bean. Amazing as it may seem, it is within the realm of possibility that this leguminous plant will enter into the manufacture of automobile parts, window frames, paint, adhesives, extremely light but strong plastics, printer's ink, soap, textiles, and synthetic rubber. What an effect this would have upon agriculture!

Nitrogen, phosphorus, and potassium are the three most important elements necessary to soil fertility. Chemists have succeeded in obtaining an abundant supply of the first two but not of potassium. The world's supply of soluble potassium salts is very meagre, yet Canada which imports 20,000 tons of potash fertilizer annually has millions of tons of feldspar, a mineral rich in potassium. However, as yet, no one has discovered a method of making a potash fertilizer from this abundant mineral. This is a task awaiting the research chemist and its accomplishment would mean much to Canada and Canadians. Agricultural chemists are beginning to realize the need of adding other elements to the soil. Food grown in soil containing added components will be richer in mineral and vitamin content and so will help to improve the health of the consumer.

What about the nature of the plants of the future? Colchichine, a substance developed in the laboratory, when administered to plants, increases their size enormously and improves their vitamin content. With new, but similar drugs, shall we grow strawberries as big as our largest apples or pumpkin-sized onions? It is within the realm of possibility that new varieties of plants may be produced through the action of drugs yet to be discovered.

The industrial research chemist has predicted the production of remarkable substances which will revolutionize our present standards of living. Unbreakable, floating glass; non-combustible wood; roof

tiles, flooring and wall board of synthetics; plastic automobiles; wood-plastic laminations stronger than steel; all these are more than mere dreams. The spinning and weaving industry with its hundreds of thousands of looms is in danger of becoming obsolete with the discovery of a new plastic capable of binding cotton or other fibre material into a cloth.

There is a possibility that crumpled automobile fenders in the future may be smoothed out with a hot iron because of the material used in their manufacture. A new synthetic rubber may find a place in impregnating paper bags and so replace metal for packaging "canned" foods. On the other hand, there is a distinct possibility that tires of the future will not be made of rubber!

In the field of medicine, man is fast gaining control over numerous diseases that have exacted such a toll in human suffering. Sulpha drugs and penicillin are now manufactured on a large scale, and new and more powerful chemicals obtainable from soil bacteria are promised. Most of the vitamins can now be made synthetically and there is a real possibility that new ones will be discovered to play their parts in improving health.

From the foregoing, it is obvious that the chemist has untold possibilities before him, and that the study of chemistry is of major importance. Some knowledge of chemistry is either valuable or absolutely necessary in almost any field of research, and the chemist also finds a knowledge of other sciences important. He would not think of conducting research in medicine or food production without a basic knowledge of animals and plants, or of undertaking atomic research without a knowledge of physics and mathematics. The world of chemistry requires an increasing number of scientific workers, and the personnel of science is today far too meagre for the stupendous labours ahead. For those who are willing to work, there is no limit to the opportunities open in the various fields of chemistry.

Review Exercises

A

In Chapter 15 all the word equations, linked with the initial portion of the course, were collected in order that balanced chemical equations could be written. The following list represents some of the important reactions studied in the later portion of the course. In each case, write a word equation, followed by a balanced chemical equation.

1. A solution of sodium hydroxide neutralizes hydrochloric acid.
2. Potassium hydroxide solution is added to sulphuric acid.
3. Nitric acid on a desk top is neutralized with limewater.
4. Ammonium hydroxide is added to hydrochloric acid.
5. Red lead is reduced with powdered charcoal.
6. Cupric oxide is reduced with finely-divided coke.
7. Charcoal is burned in oxygen.
8. A piece of marble is intensely heated.
9. Baking soda is heated.
10. The laboratory preparation of carbon dioxide gas.
11. The action of three different acids on three different carbonates.
12. Carbon dioxide is the anhydride of carbonic acid.
13. The unstable character of carbonic acid.
14. Burning magnesium is placed in a jar of carbon dioxide.
15. The chemical changes occurring when carbon dioxide gas is bubbled in excess through limewater.
16. The action that takes place in a "soda-acid" fire extinguisher.
17. The production of carbon monoxide gas in a coal-burning furnace.
18. The laboratory preparation of carbon monoxide.
19. The combustion of carbon monoxide gas.
20. The reducing action of carbon monoxide on ferric oxide.
21. The laboratory preparation of acetylene gas.
22. The complete combustion of acetylene.
23. The incomplete combustion of acetylene.
24. The industrial preparation of "water gas".
25. The laboratory preparation of hydrogen sulphide gas.
26. The complete combustion of hydrogen sulphide.
27. The incomplete combustion of hydrogen sulphide.
28. The reduction of sulphur dioxide by hydrogen sulphide gas.
29. A water solution of hydrogen sulphide is allowed to stand.
30. Hydrogen sulphide gas is bubbled into water solutions of the following salts: (a) cupric chloride; (b) lead nitrate; (c) zinc sulphate; (d) silver nitrate; (e) arsenic trichloride; (f) antimonious chloride; (g) lead acetate.
31. Hydrogen sulphide tarnishes silver.
32. The laboratory preparation of sulphur dioxide gas.
33. The industrial preparation of sulphur dioxide by roasting iron pyrites.
34. A solution of potassium permanganate is decolorized by the reducing action of sulphur dioxide gas.

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35. The bleaching action of sulphur dioxide on certain coloured substances.
36. Sulphurous acid is exposed to the oxygen of air.
37. The commercial preparation of sulphuric acid by the "contact process":
 - (a) the formation of sulphur dioxide;
 - (b) the formation of sulphur trioxide;
 - (c) the absorption of this sulphur trioxide by concentrated sulphuric acid;
 - (d) the fuming sulphuric acid (oleum) formed is diluted with water.
38. The action of concentrated sulphuric acid on cane sugar.
39. The action of hot, concentrated sulphuric acid on (a) copper, (b) zinc.
40. A chemical test for the identification of a soluble sulphate.
41. A chemical test for the identification of a soluble sulphite.
42. (a) The ionization of sodium chloride when dissolved in water. (b) The electrolysis of sodium chloride brine to show (i) primary and (ii) secondary products.
43. The commercial preparation of sodium bicarbonate (baking soda).
44. The commercial preparation of sodium carbonate (washing soda) crystals.
45. The action of concentrated sulphuric acid on common salt: (a) when gently heated, (b) when an excess of common salt is used and intense heat is applied.
46. The action of hydrochloric acid on (a) zinc, (b) iron, (c) aluminum.
47. The action of hydrochloric acid on sodium sulphite.
48. The action of hydrochloric acid in cleaning rust from iron.
49. The action of ammonia gas on hydrogen chloride gas.
50. The identification of a soluble chloride using a solution of silver nitrate.
51. The laboratory preparation of chlorine gas using (a) manganese dioxide and hydrochloric acid; (b) a mixture of sodium chloride and manganese dioxide moistened with concentrated sulphuric acid; (c) potassium permanganate and hydrochloric acid.
52. The laboratory preparation of bromine.
53. The laboratory preparation of iodine.
54. The direct union of chlorine gas with (a) sodium, (b) copper, (c) phosphorus, (d) antimony.
55. The action of chlorine gas on warm turpentine.
56. The bleaching (germicidal) action of chlorine gas.
57. The composition of freshly-prepared chlorine water.
58. (a) The bleaching action of freshly-prepared chlorine water; (b) The absence of any bleaching effect when chlorine water has been allowed to stand in sunlight for several days.
59. The commercial preparation of bleaching powder.
60. The liberation of chlorine from bleaching powder.
61. Chemical tests for the identification of chlorides, bromides, and iodides using (a) a solution of silver nitrate; (b) chlorine gas, or a freshly-prepared solution of chlorine in water; (c) liquid bromine, or a freshly-prepared solution of bromine in water.
62. The Downs process for making sodium.
63. The Castner process for preparing sodium.
64. (a) Metallic sodium tarnishes in air. (b) A piece of sodium is ignited and then placed in a jar of oxygen. (c) Sodium reacts with water.
65. Water is added to sodium peroxide.
66. The decomposition of sodium nitrate when heated.
67. The laboratory preparation of ammonia gas.

68. Ammonia gas is bubbled into water.
69. The unstable character of ammonium hydroxide.
70. Ammonia gas is burned in oxygen.
71. The industrial synthesis of ammonia by the Haber process.
72. The cyanamide process to prepare (a) calcium cyanamide; (b) to release ammonia.
73. A chemical test for the identification of an ammonium compound.
74. The laboratory preparation of nitric acid.
75. The preparation of nitric acid (a) by the oxidation of nitrogen at high temperatures; (b) by the oxidation of ammonia (Ostwald process).
76. The unstable character of nitric acid when heated, or exposed to sunlight.
77. The oxidizing action of dilute nitric acid on zinc.
78. (a) The action of dilute nitric acid on copper. (b) The action of concentrated nitric acid on copper.
79. The manufacture of potassium nitrate (ordinary saltpetre) from hot, concentrated solutions of potassium chloride and sodium nitrate.
80. The laboratory preparation of nitrous oxide gas.
81. The laboratory preparation of nitric oxide gas.
82. The effect of exposing a bottle of nitric oxide to air.
83. The heating of limestone in a kiln.
84. The slaking of quicklime by the addition of water.
85. The "air slaking" of quicklime.
86. The hardening of (a) mortar, (b) plaster. (c) whitewash.
87. The manufacture of plaster of Paris from gypsum.
88. The "setting" of plaster of Paris when water is added.
89. The industrial production of calcium carbide.
90. The removal of temporary hardness in natural waters (a) by boiling; (b) by (i) adding washing soda; (ii) adding slaked lime; (iii) "wasting" soap.
91. The removal of permanent hardness in natural waters: (a) by adding washing soda; (b) by "wasting" soap.

B

1. A solid, or a mixture of solids, is heated. No liquid is added. A chemical change takes place and a gas is produced. (a) Name three different gases that may be produced in this way. (b) Name the solid or solids used to produce each gas named in your answer to (a), and in each case specify the gas produced. (c) Write the equation for the chemical reaction involved in each case.
2. (a) Describe what is observed when (i) sodium is dropped into cold water; (ii) hydrogen is burned in air and the flame directed against a cold object; (iii) silver nitrate solution is added to a solution of common salt; (iv) a bottle with some wet steel wool packed tightly in the bottom, is inverted over water; (v) dilute hydrochloric acid is added to a small piece of ferrous sulphide. (b) Name all the substances produced in any four of the above experiments.
3. Potassium chloride, mercuric oxide, hydrochloric acid, ammonium chloride, bromine, magnesium oxide, phosphorus pentoxide, mercury, tincture of iodine, nitrous oxide, limewater, calcium chloride, washing soda crystals, nitrogen, ammonia.

From the above list of substances select and name (a) two substances which are solids at ordinary temperature and pressure; (b) two substances which are liquids at ordinary temperature and pressure; (c) two substances which are

gases at ordinary temperature and pressure; (d) two substances which are elements; (e) two substances which are chemical compounds; (f) two substances which are solutions; (g) two solids which undergo a change when exposed to the air at the same temperature for some time. In answering, state the change which takes place in each example selected.

4. Briefly describe experiments, one for each, to demonstrate the following: (a) washing soda crystals effloresce in dry air; (b) carbon dioxide affects the burning of a candle; (c) phosphorus burns in oxygen to form an acid anhydride; (d) tomato juice is a mechanical mixture.

5. (a) Write the names and the formulae for two oxides which dissolve in water to give acid solutions. (b) Write the names and the formulae for two oxides which dissolve in water to give basic solutions. (c) Write four balanced equations for the reactions suggested in (a) and (b). (d) Indicate the valence of the element combined with oxygen in each of the four examples given in your answers to (a) and (b).

6. Using a labelled diagram to illustrate your answer, describe the method of operation when using the following pieces of apparatus: (a) a laboratory still and condenser; (b) a cell for the electrolysis of water; (c) a Kipp for generating hydrogen; (d) a commercial fire extinguisher of the soda-acid type.

7. The following is a list of observations made on several substances prepared in the laboratory: (a) a colourless gas on being bubbled through limewater causes a milky precipitate; (b) a colourless gas with a nauseating odour darkens filter paper moistened with lead nitrate solution; (c) a greenish-yellow gas has an irritating, unpleasant odour; (d) a colourless gas burns with a pale-blue flame, producing water; (e) a colourless liquid reacts with copper turnings, liberating a brown gas.

(i) Name each of the gases described above and the substances commonly used in the laboratory to produce each of them. (ii) Write a balanced equation for each of the reactions suggested.

8. Describe experiments, one for each, to demonstrate the following statements: (a) washing soda effloresces; (b) sulphur dioxide is an acid anhydride; (c) carbon is a reducing agent; (d) iodine sublimes on being heated.

9. The following is a list of laboratory experiments: (a) Magnesium is strongly heated in an open crucible. (b) Marble is strongly heated in an open crucible. (c) A mixture of manganese dioxide and potassium chlorate is heated in a test-tube. (d) A mixture of manganese dioxide and hydrochloric acid is heated in a test-tube. (e) A piece of calcium is dropped into water. (f) A piece of calcium carbide is dropped into water. (g) Zinc is placed in a mixture of sulphuric acid and water. (h) Copper is strongly heated with concentrated sulphuric acid.

(i) In each of the above experiments name the new substance or substances produced. (ii) Describe what is observed in each case listed. (iii) Write balanced equations for each reaction.

10. Give a distinctive test for (a) a volatile potassium compound; (b) a soluble chloride; (c) a soluble nitrate; (d) a soluble iodide.

11. State two specific commercial uses for each of the following: hydrogen, calcium carbonate, carbon dioxide, potassium nitrate, sodium hydroxide, ammonia.

12. (a) Describe what is observed when the following experiments are performed: (i) About 1 cc. of red lead is left in chlorine water (a solution of chlorine in water) for several hours, and the mixture is shaken from time to time.

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(ii) Water is dropped into a test-tube containing calcium carbide and a lighted match is held to the mouth of the test-tube. (iii) Powdered potassium iodide is mixed with manganese dioxide. The mixture is moistened with concentrated sulphuric acid and heated in a vertical container while a cold watch-glass is inverted over the mouth of the container. (iv) A small piece of potassium is dropped into cold water. (v) A clean test-tube is filled one-third full of sodium thiosulphate crystals. A few drops of water are added and the contents of the tube are carefully heated at about 80°C . until no further change is observed. The tube and contents are then carefully cooled, after which a thermometer whose bulb has been rubbed with a sodium thiosulphate crystal is thrust into the liquid. (b) Name the substances formed in each of the experiments listed. (c) Write chemical equations for the reactions in (ii), (iii), and (iv).

13. Explain the meaning of each of the following statements: (a) when sodium is dropped on water there is an exothermic reaction; (b) sodium hydroxide is deliquescent; (c) the valence of magnesium is two; (d) carbon monoxide is a reducing agent.

14. Write formulae for sodium sulphide, calcium chlorate, Epsom salt (magnesium sulphate heptahydrate), nitrous oxide, potassium nitrite, sodium bicarbonate, ammonium carbonate.

15. (a) Explain the apparent loss in weight when wood burns and the gain in weight when a metal burns. (b) Iron and sulphur are mixed and then strongly heated. Use this experiment to explain the terms element, mixture, and compound.

16. State how you would distinguish between the substances named in each of the following pairs: (a) sodium and potassium; (b) potassium bromide and potassium iodide; (c) calcium carbonate and calcium oxide; (d) hard water and soft water; (e) dilute nitric acid and dilute sulphuric acid.

17. (a) Describe what is observed when the following experiments are performed: (i) A deflagrating spoon containing burning sulphur is thrust into a jar of oxygen which is immediately closed. After all action has ceased, a small quantity of water is poured into the jar, which is then shaken well, and bromthymol blue or neutral litmus is added to the liquid. (ii) Concentrated sulphuric acid is added slowly to powdered sodium chloride in a Florence flask which is provided with a delivery tube. The delivery tube is led into a jar of cold ammonia gas. (iii) Marble (limestone) is heated in a blowpipe or blast flame, and the resulting substance is powdered and dropped into a small quantity of water. The liquid is then filtered and carbon dioxide is passed into the filtrate until no further change is observed. (iv) A mixture of ammonium sulphate and slaked lime is heated in a test-tube provided with a delivery tube which projects into some water containing litmus. (v) A moistened, bright coin is held over a test-tube in which hydrochloric acid has been added to pieces of ferrous sulphide. (b) Name all of the substances produced in each of the above experiments.

18. State how you would distinguish experimentally (a) sulphur dioxide and hydrogen chloride; (b) sodium nitrate and potassium nitrate.

19. Name substances, two for each, which can be used satisfactorily (a) for bleaching cotton; (b) for softening water; (c) in the cooling unit of an electric refrigerator; (d) as chemical fertilizers.

20. Explain the meaning and give an example of each of the following: hydrate, exothermic reaction, reducing agent, saturated solution, element.

21. Explain why chlorine bleaches damp litmus paper but does not bleach

dry litmus paper.

22. How would you distinguish by chemical means between (a) nitrogen and carbon dioxide; (b) hydrogen and carbon monoxide; (c) oxygen and nitrous oxide; (d) dilute solutions of nitric and sulphuric acids; (e) sodium carbonate and sodium chloride?

23. State two commercial uses for each of the following: hydrogen, calcium carbonate, carbon dioxide, potassium nitrate, sodium hydroxide, ammonia, calcium chloride, sodium bicarbonate, chlorine, acetylene, sulphur dioxide.

24. If 3 litres of ammonia gas measured at 0° C. and 760 mm. are added to 3 litres of hydrogen chloride gas measured at 25° C. and 750 mm., what will be the volume of the remaining gas measured at 20° C. and 760 mm.?

25. The following observations were made on five laboratory experiments: (a) A white crystalline powder is mixed with an equal volume of manganese dioxide, and then moistened with sulphuric acid. When this mixture is heated in a test-tube, a purplish gas is given off. (b) A white crystalline powder is strongly heated and a colourless gas that causes a glowing splint to burst into flame is given off. (c) A white or grayish-white solid is finely ground, placed in a crucible, and strongly heated by means of a blast lamp. A colourless gas that forms a precipitate when passed through limewater is produced. (d) A white powder is mixed with water and a small amount of sulphuric acid is added. A moist coloured cloth is bleached by the gas produced. (e) Iron filings and a yellow powder are mixed together, placed in a test-tube, and heated gently. When hydrochloric acid is added to the substance formed, a gas with a nauseating odour is given off.

(i) Name each of the gases described above and the powder which was used to prepare each of them. (ii) Write chemical equations for all the suggested reactions.

26. "Experiments with chlorine, bromine, and iodine show remarkable similarities among the three elements in some particulars and striking gradations of properties in others." (a) Point out these similarities and gradations of properties. (b) You are given a powder known to be potassium chloride, potassium bromide, or potassium iodide. Describe the experiments you would perform to establish the identity of the powder.

27. You are given a gas to identify and you know it is one of the following: oxygen, hydrogen, nitrogen, chlorine, carbon dioxide, carbon monoxide, ammonia, methane, hydrogen chloride, nitrogen dioxide, hydrogen sulphide, sulphur dioxide. (a) First you notice that the given gas is colourless. As a result of this observation some of the possible gases may be eliminated. Make a list of those remaining to be considered. (b) You then collect some of the gas in a test-tube and apply a lighted match. The gas burns. This result eliminates more of the gases. Make a list of those still remaining to be considered. (c) You shake the product of combustion from (b) with lime-water. There is a white precipitate. Which gases now remain to be considered? (d) You ignite the gas in a dry cylinder. There is no deposit of moisture on the glass. What gas was it?

28. Give an account of sodium and potassium under the following headings: (a) chief sources; (b) physical properties of these elements; (c) preparation of the hydroxides; (d) properties of the aqueous solutions of the hydroxides; (e) chief uses of the nitrates.

29. A certain gaseous substance is known to be a compound of nitrogen and

oxygen. What experiments would be necessary in order to determine the formula to be assigned to the gas?

30. (a) Give the formulae for baking soda, washing soda, Chile saltpetre, ordinary saltpetre, muriatic acid, plaster of Paris, gypsum, limestone, potassium permanganate, acetic acid, calcium carbide, calcium bicarbonate, sodium bisulphite. (b) Write the formulae for: potassium sulphide, calcium bromide, nitrous oxide, sodium perchlorate, carbon disulphide, carbon tetrachloride, ammonium phosphate, potassium chlorite, calcium hypochlorite. (c) Write equations for each of the following experiments: (i) Dilute sulphuric acid is neutralized with ammonia. (ii) Acetylene is burned in air. (iii) A solution of chlorine is added to a solution of potassium bromide. (iv) Potassium iodide is heated with manganese dioxide and sulphuric acid.

31. (a) What are the industrial uses of sulphur? (b) How could you detect the presence of hydrogen sulphide in coal gas? (c) Describe an experiment showing the reducing action of sulphur dioxide.

32. (a) What are the general characteristics of bases? (b) Write equations for the reaction of calcium oxide, sodium oxide, and ammonia, respectively, with each of sulphuric acid and nitric acid.

33. Ten litres of each of the following gases are burned in oxygen: carbon monoxide, hydrogen, hydrogen sulphide, methane. Find in each case, the volume of oxygen needed, measured at standard temperature and pressure. Name the products of combustion in each case.

34. How would you show experimentally (a) that a certain solution of sugar is saturated, (b) that water contains dissolved air, (c) that the atmosphere contains water, (d) that carbon dioxide is present in the atmosphere, but in exceedingly small amounts?

35. (a) State how each of the following substances would be affected by being exposed to the air: (i) ammonium hydroxide solution; (ii) concentrated sulphuric acid; (iii) slaked lime; (iv) washing soda crystals.

(b) State how you would prepare (i) a supersaturated solution of "hypo"; (ii) the three allotropic forms of sulphur from roll sulphur; (iii) ozone from oxygen.

36. (a) Calculate the percentage of water by weight of hydration in ammonium alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. (b) The bones of an average adult person weigh approximately 24 pounds and contain approximately 48% calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. Calculate the weight of phosphorus present in the skeleton of the average adult.

37. Describe how you would obtain (a) pure dry salt from a mixture of sodium chloride and sand; (b) pure ammonia gas from a large Florence flask filled with ammonia gas and air; (c) pure sulphur from a mixture of iron filings and flowers of sulphur; (d) pure water from sea-water.

38. (a) What information is expressed in a chemical equation? (b) $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$. If this reaction takes place when calcium carbide reacts with water, indicate the weight and volume relations expressed by it. (c) If an acetylene bicycle lamp contains 128 grams of calcium carbide and sufficient water, how long would it burn, if the lamp consumed 10 litres of acetylene per hour, the gas being measured at standard temperature and pressure?

39. Classify the following substances as oxidizing agents or reducing agents and justify your classification discussing one experiment for each: nitric acid,

sulphurous acid, carbon, chlorine.

40. If 500 cc. of a solution of sodium hydroxide containing 32 grams of pure NaOH per litre is needed to neutralize completely 100 cc. of sulphuric acid solution, find the weight of pure acid per litre in the sulphuric acid solution.

41. Two compounds have the following composition: (a) phosphorus 56.36%, oxygen 43.64%; (b) phosphorus 43.65%, oxygen 56.35%. Show how these facts illustrate the Law of Multiple Proportions.

42. (a) If 10 grams of "hypo", $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, were thoroughly dehydrated, what weight of the anhydrous salt would remain? (b) Two substances, one a gas and the other a volatile liquid, were found on analysis to have the same percentage composition by weight: carbon, 92.307%; hydrogen, 7.693%. In the case of the gas, the density referred to hydrogen was 13, and in the case of the volatile liquid was 39. What are the true (molecular) formulae for these two substances?

43. (a) The equivalent weight of zinc is 32.7. What volume of hydrogen under standard conditions will be displaced by 4 grams of this metal when dissolved in an acid? (b) What weight of potassium chlorate, 98% pure, is necessary to produce 2.28 litres of oxygen, collected over mercury at 21° C. and 753 mm.?

44. Give a distinguishing test for each of the following gases: hydrogen chloride, sulphur dioxide, oxygen, hydrogen, chlorine, carbon dioxide, ammonia, carbon monoxide.

45. Give the name for aqueous solutions of: hydrogen chloride, hydrogen sulphide, carbon dioxide, sulphur dioxide, ammonia, magnesium oxide, sulphur trioxide, quicklime, chlorine, bromine.

46. Define each of the following: valence, atomic weight, molecular weight of an element, simplest formula, molecular formula, acid, base, neutralization, gram-molecular weight, gram-molecular volume, element, chemical compound, solution, mechanical mixture, unsaturated solution, saturated solution, super-saturated solution, fractional distillation, destructive distillation, hydrate, efflorescence, deliquescence, catalyst, radical, normal salt, acid salt, anhydrous salt, acid anhydride.

47. State each of the following laws used in chemistry: Boyle's, Charles's, Avogadro's, Gay-Lussac's, Henry's, Conservation of Mass, Definite Proportions, Multiple Proportions, Combining Weights.

48. (a) What volume of carbon dioxide at 0° C. and 1 atmosphere would be produced by the action of an excess of hydrochloric acid on 2 grams of calcium carbonate? (b) What volume would this quantity of carbon dioxide occupy at 27° C. and a pressure of 2 atmospheres? (c) What weight of calcium chloride would be formed in this reaction?

Appendix

A. IMPORTANT UNITS IN THE METRIC SYSTEM

Length

10 millimetres (mm.)	=	1 centimetre
10 centimetres	=	1 decimetre (dm.)
10 decimetres	=	1 metre (m.)
1000 metres	=	1 kilometre (km.)

Mass (Weight)

10 milligrams (mg.)	=	1 centigram (cg.)
10 centigrams	=	1 decigram (dg.)
10 decigrams	=	1 gram (gm.)
1000 grams	=	1 kilogram (kg.)

Volume

1000 cubic centimetres (cc.)	=	1 litre (l.)
1 cc.	=	.001 litres = 1 millilitre (ml.)

While a cubic centimetre and a millilitre have not exactly the same value, the variation is so slight that for practical purposes these two units may be considered identical.

B. RELATIONSHIP OF SOME ENGLISH AND METRIC UNITS

1 inch (in.)	=	2.54 centimetres
1 metre	=	39.37 inches
1 kilometre	=	0.62 miles
1 pound (lb.) Avoirdupois	=	453.6 grams
1 ounce (oz.) Avoirdupois	=	28.35 grams
1 kilogram	=	2.20 pounds
1 litre	=	0.88 quarts (British)
1 cubic foot (cu.ft.)	=	28.32 litres

C. GENERAL RULES FOR SOLUBILITY

1. All *sodium*, *potassium*, and *ammonium* compounds are soluble in water.
2. All *nitrates*, *chlorates*, and *acetates* are soluble.

3. All *chlorides*, *bromides*, and *iodides* are soluble except those of *silver*, *lead*, and *mercury* (mercurous).

4. All *sulphates* are soluble except those of *barium*, *lead* *calcium* (slightly), *silver* (slightly).

5. All *hydroxides* are insoluble except those of *sodium*, *potassium*, *ammonium*, *calcium*, and *barium*.

6. All *sulphides* are insoluble except those of *sodium*, *potassium*, *ammonium*, *calcium*, and *barium*.

7. All *carbonates*, *phosphates*, and *silicates* are insoluble except those of *sodium*, *potassium*, and *ammonium*.

There are a few unimportant exceptions to these general rules.

D. SOME COMMON NAMES OF SUBSTANCES AND THEIR FORMULAE

COMMON NAME	FORMULA
Alum	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Ammonia Water	NH_4OH
Aqua regia	HCl (4 volumes) + HNO_3 (1 volume)
Baking powder	$NaHCO_3$ + starch + an acid-acting ingredient
Baking soda	$NaHCO_3$
Bleaching powder	$CaOCl_2$
Blue vitriol (bluestone)	$CuSO_4 \cdot 5H_2O$
Bone black	C
Caustic potash	KOH
Caustic soda	NaOH
Chile saltpetre	$NaNO_3$
Chloride of lime	$CaOCl_2$
Coke	C
Common salt	Na Cl
Cream of tartar	$KHC_4H_4O_6$
Dextrose (glucose)	$C_6H_{12}O_6$
Diamond	C
Dry ice	CO_2 (solid)
Epsom salts	$MgSO_4 \cdot 7H_2O$
Flowers of sulphur	S
Glauber's salt	$Na_2SO_4 \cdot 10H_2O$
Glucose (dextrose)	$C_6H_{12}O_6$
Glycerine (glycerol)	$C_3H_5(OH)_3$
Grain alcohol (ethyl)	C_2H_5OH
Graphite	C

COMMON NAME	FORMULA
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Household ammonia	NH_4OH
Hypo (crystals)	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
Lampblack	C
Laughing gas	N_2O
Lime (hydrated)	$\text{Ca}(\text{OH})_2$
Lime (quicklime)	CaO
Lime (slaked)	$\text{Ca}(\text{OH})_2$
Limestone	CaCO_3
Limewater	$\text{Ca}(\text{OH})_2$
Lye	NaOH
Marble	CaCO_3
Marsh gas (methane)	CH_4
Methyl alcohol (methanol)	CH_3OH
Muriatic acid (hydrochloric)	HCl
Naphthalene (moth balls)	C_{10}H_8
Oil of vitriol	H_2SO_4
Plaster of Paris	$(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$
Quicklime	CaO
Quicksilver (mercury)	Hg
Sal ammoniac (ammonium chloride)	NH_4Cl
Sand	SiO_2
Slaked lime	$\text{Ca}(\text{OH})_2$
Soap (sodium stearate)	$\text{C}_{17}\text{H}_{35}\text{COONa}$
Soda ash	Na_2CO_3
Sugar (sucrose)	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Vinegar (acetic acid)	$\text{HC}_2\text{H}_3\text{O}_2$
Washing soda (crystals)	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Wood alcohol	CH_3OH

E. GENERAL PROPERTIES OF METALS AND NON-METALS*Metals***PHYSICAL PROPERTIES**

1. Good conductors of heat.
2. Good conductors of electricity.
3. Greyish metallic lustre, except copper (red) and gold (yellow).
4. Malleable. (Gold may be pounded into sheets .0001 cm. thick.)
5. Ductile. (Wire may be produced weighing .000005 gm/cm.)

CHEMICAL PROPERTIES

1. All form oxides either by direct combination or by some intermediate reaction.
2. Metallic oxides are basic anhydrides.
3. The more active metals (those above Hydrogen in the activity series) react with acids liberating hydrogen.
4. The more active metals react with water forming hydrogen and a base.
5. Metals react with non-metals to form salts.

*Non-Metals***PHYSICAL PROPERTIES**

1. Poor conductors of heat.
2. Poor conductors of electricity, except graphite and selenium.
3. Vary considerably in colour; sulphur (yellow), phosphorus (white or yellow or red), chlorine (greenish-yellow), bromine (brownish-red), iodine (steel-grey with violet vapour).
4. Not malleable.
5. Not ductile.

CHEMICAL PROPERTIES

1. All form oxides either by direct combination or by some intermediate reaction.
2. Non-metallic oxides are acid anhydrides.
3. Only the most active non-metals react with water and when they do, they form acids and liberate oxygen.
4. Non-metals react with metals to form salts.

F. THE ELEMENTS

ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT	ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Actinium	Ac	89	227.0	Molybdenum	Mo	42	95.95
Aluminum	Al	13	26.98	Neodymium*	Nd	60	144.27
Americium	Am	95	(243)	Neon	Ne	10	20.183
Antimony	Sb	51	121.76	Neptunium	Np	93	(237)
Argon	A	18	39.944	Nickel	Ni	28	58.69
Arsenic	As	33	74.91	Niobium	Nb	41	92.91
Astatine	At	85	(210)	Nitrogen	N	7	14.008
Barium	Ba	56	137.36	Osmium	Os	76	190.2
Berkelium	Bk	97	(245)	Oxygen	O	8	16.0000
Beryllium	Be	4	9.013	Palladium	Pd	46	106.7
Bismuth	Bi	83	209.00	Phosphorus	P	15	30.975
Boron	B	5	10.82	Platinum	Pt	78	195.23
Bromine	Br	35	79.916	Plutonium	Pu	94	(242)
Cadmium	Cd	48	112.41	Polonium	Po	84	210.0
Calcium	Ca	20	40.08	Potassium	K	19	39.100
Californium	Cf	98	(246)	Praseodymium*	Pr	59	140.92
Carbon	C	6	12.010	Promethium	Pm	61	(145)
Cerium*	Ce	58	140.13	Protactinium	Pa	91	231.0
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222.0
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Copper	Cu	29	63.54	Rubidium	Rb	37	85.48
Curium	Cm	96	(243)	Ruthenium	Ru	44	101.7
Dysprosium*	Dy	66	162.46	Samarium*	Sm	62	150.43
Erbium*	Er	68	167.2	Scandium	Sc	21	44.96
Europium*	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.09
Francium	Fr	87	(223)	Silver	Ag	47	107.880
Gadolinium*	Gd	64	156.9	Sodium	Na	11	22.997
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulphur	S	16	32.066
Gold	Au	79	197.2	Tantalum	Ta	73	180.88
Hafnium	Hf	72	178.6	Technetium	Tc	43	(99)
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium*	Ho	67	164.94	Terbium*	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.91	Thulium*	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.92
Lanthanum*	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium*	Lu	71	174.99	Ytterbium*	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

*Rare Earths

Atomic weight in brackets denotes mass number of the isotope of longest known half-life.

G. COMPARISON OF ORGANIC AND INORGANIC COMPOUNDS.

	ORGANIC COMPOUNDS	INORGANIC COMPOUNDS
1. Constituent elements	Carbon always; hydrogen usually; oxygen often; nitrogen, halogens, sulphur, phosphorus, etc.	All elements (except inert gases) including carbon in carbonates, and carbides.
2. Number of compounds	About 1,000,000.	About 60,000.
3. Molecular weights	From 16 (CH_4) to many millions (proteins).	From 7 (LiH) to about 4000.
4. Melting and boiling points	Usually low.	Usually high.
5. Effect of heat	Practically all decompose at higher temperatures (above $350^\circ\text{C}.$).	Usually resist decomposition.
6. Solubility	Most have low solubility in water and high solubility in organic liquids.	Many are soluble in water but not soluble in organic liquids.
7. Ionization	Most are non-electrolytes; if any ionize, usually they are weak electrolytes.	Usually good electrolytes.
8. Valence	Covalence almost always.	Electrovalence and covalence.
9. Isomerism	Common.	Very rare.

Answers

Chapter 4 (page 30)

18. 11.11% 19. (a) 39.15% (b) 60.85%

Chapter 5 (page 41)

20. 22.92% oxygen, 77.08% nitrogen

Chapter 6 (page 55)

B

1. 1.98 gm. 2. 8:1 3. 88.81% oxygen, 11.19% hydrogen

Chapter 7 (page 70)

B

1. 11.08:88.92 2. (a) 8 gm., (b) 9 gm., (c) 1 gm., (d) 1:8
3. 88.81% oxygen, 11.19% hydrogen 4. 2:1
5. 12 ml. oxygen 6. 11.3 cc. oxygen
7. 6 cc. oxygen, 79 cc. nitrogen

Chapter 8 (page 78)

B

1. 14.49 gm. 2. 34.7 gm. in 100 gm. water
3. 123.99 gm. in 100 gm. water

Chapter 10 (page 99)

B

1. 429.7 cc.
2. (a) 238.55 cc., (b) 468.49 cc., (c) 4.15 l., (d) 61.8 l.,
(e) 2.45 cu. ft.
3. (b) 273° A, 293° A, 346° A, 253° A, 0° A 4. 203.7 cc.
5. (a) 879.1 cc., (b) 10.61 l., (c) 587.64 cc., (d) 26.45 l., (e) 278.39 cc.
6. 162.21 cc.
7. (a) 151.5 cc., (b) 1375.26 cc., (c) 22.45 l., (d) 14782.3 cc.,
(e) 9.04 cu. ft., (f) 194.63 cc.
8. 1.34 gm. 9. 1.22 gm.

Chapter 11 (page 115)

B

- | | | |
|--------------------------|---------------|-------------|
| 1. 12 gm. | 2. 32.61 | 3. 31.75 |
| 4. 20.1, 39.1, 27.9, 9.0 | | 5. 32.5 |
| 6. (a) 28, (b) 95.7 | | 7. (b) 31.5 |
| 11. 33.8 gm., 33.8 | 12. 33.76 gm. | 13. 71.2 |
| 14. 78.82 gm. | 15. 280 cc. | 16. 35.5 |

Chapter 12 (page 125)

B

- | | | | |
|---|--|---|-------------------------------------|
| I. 1. NO | 2. Fe ₂ O ₃ | 3. Pb ₃ O ₄ | 4. Hg ₂ O |
| 5. Al ₂ O ₃ | 6. P ₂ O ₅ , P ₂ O ₃ | 7. CH ₂ O | 8. C ₄ H ₁₀ O |
| 9. (a) NaCl, (b) FeS ₂ , (c) CaSO ₄ , (d) AgNO ₂ , (e) NaHCO ₃ , (f) NaHSO ₄ | | | |
| 10. C ₆ H ₁₂ O ₆ | 11. CH ₂ O | 12. CH ₄ | 13. C ₂ H ₆ |
| 14. PCl ₃ | 15. C ₂ H ₄ | 16. C ₂ H ₄ | 17. NH ₃ |
| 18. C ₂ H ₄ Cl ₂ | 19. Na ₂ CO ₃ .10 H ₂ O | 20. Na ₂ SO ₄ .7H ₂ O, | |
- II. 1. (a) 74.5, (b) 74, (c) 342, (d) 46, (e) 96, (f) 249.6, (g) 286, (h) 60, (i) 310, (j) 290
2. (a) potassium 31.84%, chlorine 28.98%, oxygen 39.18%, (b) iron 70%, oxygen 30%, (c) nitrogen 21.21%, hydrogen 6.06%, sulphur 24.24%, oxygen 48.48%
3. magnesium 9.76%, sulphur 13.01%, oxygen 26.02%, water 51.22%
4. (a) carbon 42.11%, hydrogen 6.43%, oxygen 51.46%, (b) phosphorus 43.66%, oxygen 56.34% (c) hydrogen 4%, carbon 32%, oxygen 64%, (d) potassium 8.23%, sulphur 13.50%, oxygen 27.00%, aluminum 5.70%, water 45.57%
5. (a) 38.71%, (b) 400 lb.
6. (a) copper 25.48%, sulphur 12.82%, oxygen 57.69%, hydrogen 4.1%, (b) 36.06%, (c) 63.94%
7. 2.55 tons
8. 1050 lb.
9. magnesium 60%, oxygen 40%
10. 38.81%
- III. 1. (a) 17 gm., (b) 17, (c) 7.59 gm., (d) 0.0759 gm., (e) 2.64 l., (f) 0.339 gm., (g) 8.5:1, (h) 0.588:1
2. 44.08 gm., 44.08, 508.8 cc., 1.47 gm., 22:1
3. 1.96 gm., 0.714 gm., 2.05 gm., 3.83 gm., 4.11 gm.
4. (a) 2.8 l., (b) 7.88 l., (c) 5.6 l., (d) 6.09 l.
5. 6.4 l.
6. (a) 64.06, (b) 33.81, (c) 36.95, (d) 4.302 gm.
7. 15.9:1
8. (a) 78, (b) 78.4, (c) 70.8
9. 31.8
10. 1.285 gm.
11. 14

Chapter 15 (page 151)**B**

- I.* 1. 7.41 gm. 2. 39.18 gm. 3. 675 gm.
 4. 127.6 gm. 5. 197.8 gm. 6. 322 lb.
 7. 7.91 gm. 8. 17.39 gm. 9. 66.7 gm.
 10. 128 gm. 11. 2.93 tons 12. (a) 177.7 lb, (b) 22.2 lb.
II. 1. (a) 64 gm., (b) 22.4 l. 2. (a) 7.99 gm.,
 (b) 0.25 gm., 2.81 l. 3. 18.75 gm., 25.9 gm.
 4. (a) 13.44 l., (b) 14.62 l. 5. 15.18 l.
 6. 1.39 gm. 7. 7.8 l. 8. 58.4 l. 9. 6.18 l.
 10. 25 cu. ft. 11. 34.7 l. 12. (a) 490 gm., (b) 144.24 l.

Chapter 16 (page 163)**B**

1. 20 gm. 2. 11.2 gm. 3. 73.13 lb.
 4. 156 gm. 5. 0.48 tons 6. 1.12 gm.

Chapter 17 (page 183)**B**

1. 1.45 gm. 2. 92.73% 3. (a) 50 gm., (b) 50 gm.
 4. 41.09 gm. 5. 44 gm., 1.52 6. 1.25 gm.
 7. (a) 20 gm., (b) 11.2 l., (c) 4.5 cc. 8. (a) 112 l., (b) two-thirds
 9. 161.5 gm. 10. 226.2 l.
 11. 1.52 times as dense as air 12. 20 litres of carbon monoxide
 13. 12.04 gm.

Chapter 18 (page 194)**B**

1. (a) 537, 600 l., (b) one-half 2. 5 l.

Chapter 19 (page 210)**B**

1. 25 gm. 2. (a) 176 gm., (b) 44.8 l. 3. 3.45 l.
 4. 5 l. 5. 17.8 gm. 6. (a) 40 l., (b) 2.54 l.

Chapter 20 (page 219)**B**

1. sodium 39.3%, chlorine 60.7% 2. sodium chloride
 3. (a) anhydrous sodium carbonate, (b) 2.9 lb.
 4. 8.96 l. 5. 12.18 l., 40 gm.

Chapter 21 (page 233)**B**

1. 38.8 gm. manganese dioxide, 28.2 gm. potassium permanganate
2. 13.54 l.
3. (a) 76.2 gm., (b) 58.8 gm.
4. (a) 8.88 gm., (b) 2.8 l., (c) 6.29 cc.
5. 50 l.

Chapter 23 (page 246)**B**

1. the baking soda, 21.3 gm. more
2. 11.5 lb.
3. (a) 35 gm., (b) 175 gm. per litre of solution

Chapter 24 (page 258)**B**

1. (a) (i) 82.35% (ii) 7.6 gm., (b) 1:1
2. 2.24 l.
3. 44.57 l.
4. 1111.8 lb.
6. (a) 30 l., (b) 20 l.
7. 125 cc.

Chapter 25 (page 269)**B**

1. 1064 lb.
2. 66.2 gm.
3. 84.3 lb.
4. (a) 20.93%, (b) 6.21%
5. 321.4 gm.
6. (a) 279.4 gm., (b) 97.1 l.

Review Exercises (page 287)**B**

24. 0.31 l. ammonia
33. 5 l., 5 l., 15 l., 20 l.
- 36 (a) 47.68, (b) 2.3 lb.
38. (c) 4 hr. 28 min. 48 sec.
40. 196 gm.
42. (a) 6.05 gm., (b) gas C_2H_2 , liquid C_6H_6
43. (a) 1.37 l., (b) 7.8 gm.
48. (a) 448 cc., (b) 246.15 cc., (c) 2.22 gm.

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APPROXIMATE ATOMIC WEIGHTS OF THE COMMON ELEMENTS

NAME	SYMBOL	ATOMIC WEIGHT	NAME	SYMBOL	ATOMIC WEIGHT
Aluminum	Al	27	Lead	Pb	207
Antimony	Sb	122	Magnesium	Mg	24
Arsenic	As	75	Manganese	Mn	55
Barium	Ba	137	Mercury	Hg	200
Bromine	Br	80	Nitrogen	N	14
Calcium	Ca	40	Oxygen	O	16
Carbon	C	12	Phosphorus	P	31
Chlorine	Cl	35.5	Potassium	K	39
Copper	Cu	63.5	Silver	Ag	108
Fluorine	F	19	Sodium	Na	23
Gold	Au	197	Sulphur	S	32
Hydrogen	H	1	Tin	Sn	119
Iodine	I	127	Zinc	Zn	65
Iron	Fe	56			

